Text-Books of Physical Chemistry

EDITED BY

SIR WILLIAM RAMSAY K.C.B., F.R.S.

AND

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A SYSTEM OF PHYSICAL CHEMISTRY

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A SYSTEM OF PHYSICAL CHEMISTRY

BY

WILLIAM C. McC. LEWIS, M.A. (R.U.I.), D.Sc. (Liv.)

BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL

IN THREE VOLUMES

VOLUME III

QUANTUM THEORY

(WITH TWO APPENDICES BY JAMES RICE, M.A., LECTURER IN PHYSICS IN THE UNIVERSITY OF LIVERPOOL)

NEW IMPRESSION

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PREFATORY NOTE.

In this volume an attempt is made to deal with some physico-chemical applications of the principles of statistical mechanics. An account is first given of the application of what is now known as the classical statistical mechanics, more particularly to the problem of the energy content of substances and its variation with temperature, on the one hand, and to the problem of radiation on the other. It will be seen that in both these branches classical statistical mechanics makes it possible for us to advance very considerably beyond the limits set by the elementary kinetic theory employed in Volume I., but at the same time it will be found that the classical statistical mechanics does not furnish us with a complete and adequate basis for all the observed phenomena. It is therefore necessary to enlarge or modify the fundamental concepts of statistical mechanics, and it is precisely with this object in view that Planck has been led to introduce the idea of quanta. Planck's quantum theory is, therefore, properly speaking, a new or modified system of statistical mechanics. It happens, however, that Planck was led to his revolutionary changes by considerations based upon the observed facts of radiation, and for this reason it is usual to speak of the quantum theory of radiation. Radiation affords, as a matter of fact, one illustration, and a very striking one, of the applicability of the new mechanics. But even the success which has attended Planck's treatment of radiation problems would scarcely have sufficed to gain for his views that prominence which they now have, had it not been for the satisfactory explanation which his theory offers at the same time for the heat content of substances and the variation of the heat content with temperature. The idea of energy quanta has been applied in recent years to other types of physico-chemical phenomena, some of which will be considered. It will be assumed, in the treatment of the subject-matter dealt with in this volume, that

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the reader is familiar with the principles of elementary kinetic theory and the principles of thermodynamics already discussed in Volumes I. and II. Such of these principles and results as may be required will be introduced therefore without further explanation.

It will be observed that there is a change of attitude in the mode of dealing with the experimental material in this volume as compared with the attitude adopted in the preceding volumes. The theoretical concepts made use of in Volumes I. and II. have become classical to a large extent, and the treatment resolves itself into a brief account of underlying principles followed by a systematic application of these principles to phenomena characteristic of systems which had attained equilibrium or were tending towards equilibrium. In the present volume, however, the underlying ideas—especially those involved in the quantum theory—have not as yet been fully accepted, at least in their present form. The position of the quantum theory is to a certain extent undefined. The physical significance of what is meant by a quantum of energy or, in a stricter sense, the quantum of action, is still vague. The present position has been summarised by Professor Bragg in the words: "His [Planck's] hypothesis is not so much an attempt to explain as a focussing of all the difficulties into one; so that, if this master difficulty is overcome, a number of others melt away". In view of what has just been said, it will be readily appreciated that many of the experimental investigations referred to in the present volume have been carried out primarily with the object of testing the validity of the quantum hypothesis itself, and as this can be done most effectively by the intensive examination of certain relatively restricted fields of research, the information available at the present time is of a somewhat detached character as compared with the variety and generality of the phenomena to the interpretation of which the simple kinetic theory and the principles of thermodynamics have been applied. For this reason, therefore, relatively little stress is laid upon the system of classification already adopted in Volumes I. and II. Naturally with the progress of investigation it will become feasible ultimately—provided the quantum hypothesis becomes generally accepted—to classify phenomena as has been done in the preceding volumes; but for the present the interest centres elsewhere, *viz.* on the validity of the underlying hypothesis itself. It is well that the reader should appreciate this state of affairs at the outset.

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CHAPTER I.

Introductory—Definitions—Probability—Statistical mechanics—Entropy and thermodynamic probability—Principle of equipartition of kinetic energy among degrees of freedom—Application of the equipartition principle to specific heats and radiation phenomena—Necessity of modifying the principle of equipartition.

Definition of Statistical Mechanics.

In what we may call classical mechanics, developed in the first instance by Newton, we become acquainted with the concepts of mass, length, and time as the fundamental physical quantities, and from these we pass on to derived concepts, such as velocity, acceleration, force, and energy, by means of which we arrive at certain principles and laws which govern physical phenomena. We say that we have "explained" a physical or chemical phenomenon, when we can restate it in terms of mechanics; that is, when we can show that the phenomenon in question is to be anticipated on the basis of a number of mechanical principles logically applied. In Volume I. we have seen how the application of mechanics to the small discrete particles, which we recognise as molecules and atoms, leads to a reasonable explanation of many physico-chemical phenomena. We have restricted ourselves, however, hitherto by certain simplifying assumptions, *i.e.* we have dealt with systems of molecules as though all the molecules possessed exactly the same value for their velocity and therefore for their kinetic energy, throughout the given mass of material, an elementary gas, for example. It is known, however, that such an assumption is by no means true. We have already indicated this in Chap. I., Vol. I., when referring to the distribution of velocities among a large number of gas molecules in terms of Maxwell's distribution law. It is true that all our experimental measurements deal with average effects, and hence by regarding every molecule as in an average state and applying the principles of mechanics, we are able to arrive at a number of very important and useful conclusions in terms of the elementary kinetic theory, for which we find experimental evidence.

This mode of treatment, however, has its limitations. Certain problems present themselves which we are quite unable to solve on the basis of the elementary kinetic theory. We have already met a number of these in Volume II., and have shown how they may be dealt with from the standpoint of thermodynamics. By way of illustration we may cite: the relation between the lowering of vapour pressure, lowering of freezing point, and rise of boiling point of a liquid as a result of

dissolving some substance in the liquid; the variation of the pressure of saturated vapour with temperature in terms of the latent heat of vaporisation; the variation of the equilibrium constant of a chemical reaction with temperature and pressure; the electromotive force of reversible cells; the relation between the heat of reaction and the chemical affinity of the process.

The laws of thermodynamics are not, however, in the first place mechanical laws—though we shall see later that the second law possesses a statistical mechanical basis—but are founded essentially upon experience; they are taken to be true, because no phenomenon or process in nature contradicts them. The characteristic feature of thermodynamical treatment is, as we have already seen, that the results obtained involve no assumption regarding the molecular structure of the system under consideration. Thermodynamical deductions are therefore perfectly general, in the sense that they hold good quite apart from specific molecular theories. It is important to point out that mechanics likewise furnishes a general mode of treatment, known as *generalised dynamics*, by which certain physico-chemical results may be obtained, the line of reasoning followed being to a certain extent analogous to thermodynamic reasoning in that no particular assumption is made regarding the molecular structure and molecular properties of the system investigated. We treat the system as a whole and do not attempt to deal with each molecule individually.

The best account of the applications of generalised dynamics to physico-chemical problems is that of Sir J. J. Thomson, in his book *Applications of Dynamics to Physics and Chemistry*. Among the problems solved by this method are: the process of evaporation (including the effect of electric charge upon the vapour pressure), the effect of an inert gas upon the value of the saturated vapour pressure; certain properties of dilute solutions, such as the lowering of the vapour pressure of the solvent by addition of solute, and the lowering of the freezing point by the solute; the deduction of the law of mass action, as expressed in the equilibrium constant, the equilibrium constant being shown to be an explicit function of the temperature; the principle of mobile equilibrium; the effect of pressure upon the freezing point of a pure liquid, and the effect of pressure upon the solubility of one substance in another; the phenomenon of adsorption; the relation between the electromotive force and "the chemical change producing it"; and other problems.

It is evident from this enumeration that the methods of generalised dynamics are of wide applicability. No attempt is made, however, to pursue this method in the present volume. Suffice it to say that generalised dynamics is based upon a general principle embodied in Hamilton's and Lagrange's functions. These "hardly require a more detailed knowledge of the structure of the system to which they are applied than the conservation of energy—the first law of thermodynamics—itself, and yet are capable of completely determining the motion of the system". Thomson compares the thermodynamical

method of treatment with that of generalised dynamics, and points out that the disadvantage of the latter compared with the former lies in the fact that, "the results are expressed in terms of dynamical quantities, such as energy, momentum, or velocity, and so require further knowledge before we can translate them in terms of the physical quantities we wish to measure, such as intensity of a current temperature, and so on; a knowledge which in all cases we do not possess. The second law of thermodynamics, on the other hand, being based on experience, does not involve any quantity which cannot be measured in the laboratory."

It is evident that generalised dynamics and thermodynamics have the great merit in common that they are essentially generalisations, and their application does not require any specialised information such as that involved in the molecular kinetic theory. What has been said therefore in Volume II. in regard to the advantage which this quality confers in the case of thermodynamics applies to much the same extent to generalised dynamics. The same disadvantage manifests itself of course, *viz.* that we do not get any clearer picture of the phenomenon in question in terms of the molecules taking part therein.

It is very necessary, however, to attempt to deal with processes which are essentially molecular in terms of the molecules themselves. The difficulty lies in the fact that when a system consists of a very large number of individuals (*e.g.* the molecules in a gas), it is quite impossible to follow out the extremely complicated path pursued by each single individual. In order to advance beyond the mode of treatment employed in the elementary kinetic theory of Volume I.—in which we got round the difficulty here presented by making the certainly untrue assumption that all molecules were identical in all respects—it is necessary to proceed in quite a different manner by introducing a new idea into mechanics which will enable us to deal with physical and chemical problems in a more exact and logical way. This new idea—the introduction of which into mechanics we owe principally to Maxwell and to Boltzmann—is embodied in the theory of Probability. When we bring probability considerations into mechanics we arrive at a mode of treatment known as *statistical mechanics*.[1] By treating molecular processes from the standpoint of statistical mechanics we are able to take account of the fact that all the molecules are not really identical but differ from one another in general in respect of velocity, direction, and energy content. The results obtained are indeed average results—as they must be if they are to be amenable to experimental test—but such results represent the combined effect of all the molecules present, due allowance being made for the lack of equality in the actual contribution made by each individual molecule to the total observed effect. This must not be taken as meaning that we have to calculate the particular position, velocity, and energy of each individual molecule at various intervals of time.

[1] For an account of this method of treatment, the reader is referred to the forthcoming work on *General Dynamics and Statistical Mechanics*, by J. Rice, M.A., which is specially adapted to the needs of physicists and chemists.

This, as already pointed out, would be quite impossible. Instead, we take advantage of the fact that the number of the molecules involved in any system with which we are concerned in physics or chemistry is so enormous that we are justified in dealing with these aggregations of molecules in a statistical manner, by introducing the principle of probability or chance into the mechanics of the process considered.

It is not proposed to attempt to give a systematic account of what may be called the principles of statistical mechanics. We are concerned mainly with one such principle, known as the principle of equipartition of kinetic energy among degrees of freedom. We shall state and apply this principle later. For the present it is necessary to familiarise ourselves with the idea of probability.

Probability.

In a purely algebraic sense probability may be defined as follows: If an event can occur in a ways and fail in b ways, each of these ways being equally likely, then the chance or probability of its occurring is $a/(a + b)$, and the chance or probability of its failing to occur is $b/(a + b)$. The sum of these two terms is necessarily unity, for the sum of the two probabilities covers all eventualities, *i.e.* the event must either happen or fail, and the sum represents certainty. It follows that mathematical probability is a fractional quantity which may be small or large, but can never exceed unity,[1] *i.e.* certainty. We may illustrate the idea by one or two examples. Suppose we have equal numbers of black and white balls inside a bag, the bag being well shaken so as to destroy any possible regularity or ordered arrangement of the balls, what is the probability or chance that, say, a white ball will be drawn from the bag? It is evident that the chance of drawing a white is the same as that of drawing a black. In other words, the probability is one half, for here $a = b$ when a is the number of white and b the number of black balls, and $a/(a + b) = 0{\cdot}5 = b/(a + b)$. It is evident that in the limit, if b becomes very small compared with a, the probability of drawing a white increases almost to a certainty, *i.e.* the fraction $a/(a + b)$ is nearly unity. We are here considering the probability of a single event occurring. Let us now consider the probability that two independent events may occur *simultaneously*. The probability in such a case is easily shown[2] to be the *product* of the probabilities of the separate events. That is, if the probability of the first event is P_1, and that of the second is P_2, then the probability P of both events occurring simultaneously is $P = P_1P_2$. Thus, if we have two bags, each containing a white balls and b black ones, the chance of drawing a single white from one bag is P_1, where $P_1 = a/(a + b)$, and the chance of drawing, say, a black ball from the other bag is P_2, where $P_2 = b/(a + b)$. The chance of drawing a white ball from the first bag

[1] Whilst this is true of mathematical probability we shall find later that there is a quantity to which the term "thermodynamic probability" has been given, this quantity being in general a large integral number.

[2] *Cf.*, for example, Hall and Knight's *Algebra*.

and simultaneously a black ball from the second bag is P where $P = ab/(a + b)^2$. This simple relation between the probabilities of two separate events and the probability that both will occur simultaneously is of great importance, and will be made use of later. Let us now consider one or two cases which possess a more distinctly chemical character.

The first which we shall take is the elementary deduction of the law of mass action given in Vol. I., Chap. III. Suppose we have a gaseous system containing n_a molecules of the substance A, and n_b molecules of the substance B. The probability of a collision between a single molecule of A and a single molecule of B is the product of the fractional concentration of each, for a collision is analogous to two events happening simultaneously, which we have just seen depends upon the product of two single chances, each of which is represented by the fractional concentration of A and B respectively.

We might regard the problem in the following way. Suppose that v is the molecular volume, *i.e.* the actual volume "occupied" by or allotted to any single molecule of A or B in the mixture. Let V be the total volume. Then, $V = (n_a + n_b)v$. Suppose for the moment that there is only one molecule of A present. Then the chance that this molecule would occupy a given volume v at a given instant of time would be the ratio of this volume to the total volume, *i.e.* the ratio v/V or $1/(n_a + n_b)$. Since there are n_a molecules of the substance A actually present, the chance that *any one* of them occupies a certain "position" or space v is given by the ratio $n_a/(n_a + n_b)$. This term is likewise the fractional concentration of the substance A. The chance that any B molecule occupies the same position is given by the expression $n_b/(n_a + n_b)$. If a molecule of A and a molecule of B occupy the same position together, this is equivalent to a collision, and hence the chance of a collision is the product of the fractional concentrations.

If the reaction required say two molecules of A to meet one molecule of B simultaneously the chance of this occurring is $\left(\frac{n_a}{n_a + n_b}\right)^2 \cdot \frac{n_b}{n_a + n_b}$ which finally takes the form: rate of collision $= k\mathrm{C}^2{}_a \,.\, \mathrm{C}_b$, for the total volume is proportional to the total number of molecules present.

These simple probability ideas may also be used to account for the influence exerted upon the collision frequency by the fact that in actual gaseous systems the molecules possess volume. Thus if r is the radius of a molecule, and l the average distance between two molecules, then when a molecule moves over a distance l it sweeps out a cylinder the cross-section of which is πr^2 and the length l. The volume of this cylinder is therefore $\pi r^2 l$. Each molecule has, on the average, a free space allotted to it which is a cube of volume l^3. Hence, as far as the radius affects the question, the chance of one molecule encountering another is $\pi r^2 l/l^3$ or $\pi r^2/l^2$. If the average velocity is u, the time of a journey between two successive collisions is l/u. Hence the number of encounters per second is $(u/l) \times$ chance of collision $= u\pi r^2/l^3$. This

quantity is obviously a constant for a particular gas at constant temperature, and hence is really included in the proportionality factor or velocity constant k.

Another illustration of the application of probability considerations is afforded by the phenomenon of coagulation of colloids by electrolytes (*cf.* Whetham, *Phil. Mag.*, [v.], **48**, 474 (1899). It is supposed that the coagulation is due solely to the neutralisation of the electrical charge of the colloid, and that one trivalent ion is exactly equivalent to 1·5 divalent ions, or to three univalent ions as far as coagulating efficiency is concerned. This is, of course, too simple an assumption, as we have already seen in the criticism of Schultze's rule (Vol. II., Chap. VIII.). Adopting this simple view of the effect, however, Whetham has shown how the numerical values obtained experimentally may be accounted for approximately. The coagulating power of an ion is defined as the reciprocal of the number of gram-equivalents of the ion which are just capable of bringing about coagulation of a given quantity of colloid. Linder and Picton found that negatively charged colloidal arsenic sulphide could be coagulated by tri-, di-, or uni-valent cations, the relative coagulating powers being in the ratios—

$$1023 : 35 : 1.$$

Let us suppose that in order to produce coagulation a certain minimum electric charge has to be brought into contact with the colloidal particle, and that such conjunctions must occur with a certain minimum frequency throughout the solution. We shall get equal charges by the conjunction of $2n$ trivalent ions, or $3n$ divalent ions, or $6n$ univalent ions, where n is any whole number. In a solution where ions are moving freely the probability that an ion is at any instant at a certain position is represented by a fraction which is proportional to the ratio between the volume occupied by the sphere of influence of the ion and the total volume of the solution. The probability is therefore proportional to the concentration of the ion, and may be written as (Ac), where A is any constant. The probability that two such ions are present together is $(Ac)^2$, and the chance that n such ions are present simultaneously at the position is $(Ac)^n$. Let us suppose that three solutions containing respectively tri-, di-, and uni-valent ions at concentrations C_3, C_2, and C_1 possess exactly the same coagulating power upon a given amount of a given colloid. Then, since the coagulating power is the same in these three cases—

$$A^{2n}C_3^{2n} = A^{3n}C_2^{3n} = A^{6n}C_1^{6n} = \text{a constant} = B.$$

Hence, the critical concentration of the trivalent ions is given by—

$$C_3 = \frac{B^{\frac{1}{2n}}}{A}$$

and similarly

$$C_2 = \frac{B^{\frac{1}{3n}}}{A} \text{ and } C_1 = \frac{B^{\frac{1}{6n}}}{A}.$$

The ratios in which these three concentrations stand to one another are—

$$C_1 : C_2 : C_3 = B^{\frac{1}{6n}} : B^{\frac{1}{3n}} : B^{\frac{1}{2n}}$$
$$= 1 : B^{\frac{1}{6n}} : B^{\frac{1}{3n}}.$$

Putting $B^{\frac{1}{6n}} = 1/x$, the ratios can be written—

$$1 : 1/x : 1/x^2.$$

These represent numbers which indicate relative concentrations of equal coagulating power. Hence the relative coagulating powers P_1, P_2, P_3 of *equal* concentrations of these three ions are given by the reciprocal of the above numbers. That is—

$$P_1 : P_2 : P_3 = 1 : x : x^2.$$

The value of x, which depends upon a number of unknown factors characteristic of the colloid considered, cannot be found on *a priori* grounds. If we take Linder and Picton's experiments into account and set $x = 32$, we get for the relative coagulating powers of univalent, divalent, and trivalent ions respectively, the values 1 : 32 : 1024. It will be seen that these numbers are of quite the same order of magnitude as those observed. Whetham predicted on this basis that the coagulating power of a tetravalent ion on the above colloid should be a large number, approximately 33000. Recent measurements have corroborated this result in so far as an extraordinarily large coagulating power is actually obtained.

The Law of Error.—It is a familiar fact in physico-chemical measurements that repetitions of a certain measurement give rise to a series of numbers which are not identical. The variations we speak of as experimental errors. The measurements are as likely to be too high as too low, that is, the errors are as often positive as negative, provided we make a very large number of determinations. (It is assumed that there is no systematic error in the apparatus or in the method of measurement.) The treatment of such results so as to obtain the most probable result, *i.e.* the most accurate determination, is a further illustration of the application of the theory of probability, somewhat more complex in nature than that hitherto considered.

Thus, it is possible to construct a probability curve, by means of the probability equation given below, which has been found to agree closely with the actual results obtained in a series of experimental determinations of a given quantity. Examples will be found in a text-book of mathematics, *e.g.* Mellor's *Higher Mathematics.* The large majority of the readings will fall very closely together, *i.e.* they will not be far removed from the true result, a smaller number of readings will be farther away on either side of the true result, and only a very small number will be much to one side or the other. This distribution of values may be represented by an expression of the form—

$$y = e^{-h^2x^2}.$$

This is known as the normal law of errors. The curve is shown in Fig. 1. x denotes the error and y the probability of its occurrence. As x increases numerically, positively, or negatively, y decreases rapidly, and when x becomes large y becomes vanishingly small. It will be observed that the curve is symmetrical.

Maxwell's Law.—Maxwell has applied the principle of probability to the problem of the distribution of velocities among the molecules of a gas, the gas being in a condition of statistical equilibrium at a uniform temperature throughout. A gas is to be regarded as a molecular chaos, the speed of any molecule varying from zero to infinity, its instantaneous value being the result of chance collisions with its neighbours. Although all values are theoretically possible for the speed of a molecule, it is found that in a system containing a large number of molecules, there are very few possessing either very great or very small

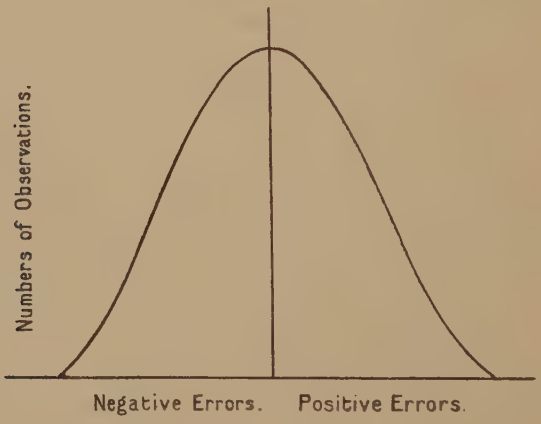

FIG. 1.

speeds. The majority of the molecules possess speeds which lie within relatively restricted limits. A numerical illustration taken from Meyer's *Kinetic Theory of Gases* is given in Appendix I.

There are, as a matter of fact, two ways of expressing Maxwell's law of distribution. One of these ways has already been stated in Chap. I., Vol. I. This way of expressing the law may be put in the form—

$$dn = \text{constant} \times \mathrm{N} \times e^{-3c^2/\bar{c}^2} \cdot c^2 \cdot dc$$

where N is the total number of molecules in the system, and dn is the number whose speeds lie between the limits c and $c + dc$. It is to be clearly understood that the speed here referred to is simply a velocity magnitude, and no restriction has been introduced as to direction of motion. The term $\bar{c}$ is known as the root-mean-square speed (or *r-m-s* speed). At a given temperature the system is characterised by a certain mean or average kinetic energy of its molecules, which is

maintained as long as the temperature is maintained constant. This average kinetic energy may be written as $\frac{1}{2}Nm\bar{c}^2$, where $\bar{c}^2$ is the sum of the squares of the velocities of all the molecules at any given instant divided by N. This *r-m-s* speed is not the same thing as the mean or average speed, which is simply the sum of all the velocities divided by N, though the two quantities are not very different numerically. The above way of expressing Maxwell's law, *i.e.* the above expression, is of the general form : $y = x^2e^{-x^2}$, which, it is to be observed, is *not* identical with the normal law of errors. The resulting curve is, in fact, not symmetrical. The alternative mode of expressing Maxwell's law wherein the curve is symmetrical, and the distinction between the two modes, is considered in Appendix I.

Maxwell's law expresses the distribution of velocities as a *continuous* function of the number of molecules present. That is, the speed of one molecule may differ by any amount (down to the infinitesimally small) from the speed of any other molecule. When we come to consider the quantum theory we shall find continuous functions replaced by discontinuous ones, *i.e.* abrupt changes in finite small steps in place of gradual change in infinitely small steps.[1]

It will be observed that Maxwell's expression involves the squares of velocities. Since the kinetic energy of a molecule depends upon the square of its velocity, it should be possible, on similar lines, to express the distribution of kinetic energy amongst the molecules constituting a gas system. If we denote by dn the number of molecules which possess kinetic energy lying between the limits E and E + dE, it can be shown that at a given temperature—

$$dn = \text{constant} \times N \times e^{-E/kT} \cdot E^{\frac{1}{2}} \cdot dE$$

where N is the total number of molecules, and k the gas constant per molecule (*i.e.* $k = R/N_0$, where R is the gas constant per gram-molecule, and N_0 is the number of molecules in 1 gram-molecule).

Further, potential energy of molecules may be considered as distributed in an analogous manner. We are here considering the potential energy of a molecule, free from intermolecular forces (as in the case of a perfect gas), the molecules being placed, however, in a field of force and the potential energy being due to this field of force, which might be conceived of as originating in some external body. A good example is the earth's gravitational field which acts on a column of gas in such a way that the molecules are more dense in the lower portion of the column than in the upper. Denoting potential energy

[1] This statement must not be taken as meaning that the distribution of kinetic energy of *translation* takes place in the discontinuous manner postulated by the quantum theory. The quantum theory applies only to energy of the vibrational or rotational type, *i.e.* motion with respect to some fixed centre of gravity. Free translational motion—such as that considered above—must be treated in a continuous manner, the velocity being capable of changing by an *infinitely* small amount.

by W, we can state that the number of molecules, the potential energy of which lies between W and W + dW, is given by—

$$dn = \text{constant} \times N \times e^{-W/kT} \cdot dW.$$

We can integrate this to obtain the number n_1 of molecules of a perfect gas (in equilibrium in a field of force at a uniform temperature) which possess potential energy W_1, that is all values from zero up to W_1.

If the total number of molecules in the system be N, the expression is

$$n_1 = N(1 - e^{-W_1/kT}).$$

If we introduce the Avogadro constant N_0, *i.e.* the number of molecules in one gram-molecule, the above expression becomes—

$$n_1 = N(1 - e^{-N_0 W_1/RT}),$$

where R is the gas constant per gram-molecule.

It follows from this that the number of molecules which possess potential energy between W_1 and infinity is $(1 - n_1)$ which is equal to

$$Ne^{-W_1/kT} \text{ or } Ne^{-N_0 W_1/RT}.$$

Distribution of Molecular Velocities and Temperature.—On the kinetic theory it is to be expected that the temperature of a gas should be expressible in purely mechanical terms. We are already familiar with the concept that temperature is measured by the kinetic energy of the molecules. In view of the distribution of velocities and therefore of kinetic energy, among molecules, as expressed in Maxwell's law, it is evident that the kinetic energy of a given individual molecule may be very different from that possessed by another molecule of the same system. Further, the kinetic energy of one and the same molecule varies from moment to moment as a result of collisions. The temperature of the system—measured in the ordinary way, by means of a thermometer—is a perfectly definite quantity for the gas system as a whole in the steady state. The temperature, in fact, is determined by the average kinetic energy. It is therefore meaningless to speak of the temperature of a single molecule in a gas. Temperature is essentially a statistical effect due to the presence of a large number of molecules each contributing its own share to the total effect. Two independent systems are at the same temperature when the average kinetic energy of each is the same. This is true whether the systems be gaseous, liquid, or solid, homogeneous or heterogeneous.

It will be appreciated at the same time that pressure is likewise a statistical effect. A single gas molecule cannot be conceived of as exerting observable pressure, though each molecule exerts a certain force against the walls of the containing vessel, the total effects of which, when numerous molecules take part, is manifested as a uniform gas pressure.

Entropy and Thermodynamic Probability.

It is proposed to indicate how the second law of thermodynamics can be deduced on the basis of statistical mechanics. This was first

demonstrated by Boltzmann. Hitherto we have regarded the second law as a law of experience, its validity depending upon the fact that no contradiction to it has been met with in nature. It is important to see that this law possesses at the same time a mechanical basis. The demonstration consists in showing the connection between the entropy of a system—the concept of entropy involving necessarily the concept of the second law—and a statistical quantity known as the *thermodynamic probability* of the system.

It is necessary to recall first of all what is meant by thermodynamical equilibrium, as stated in terms of entropy, that is as stated in terms of the second law. Planck's definition of such equilibrium is as follows (*cf.* Planck, *Theory of Heat Radiation*, English ed., p. 22): "A system of bodies of arbitrary nature, shape, and position, which is at rest and is surrounded by a rigid cover impermeable to heat, will, no matter what its initial state may be, pass in the course of time into a permanent state in which the temperature of all bodies in the system is the same. This is the state of thermodynamic equilibrium, in which the entropy of the system has the maximum value, compatible with the total energy of the system as fixed by the initial conditions. This state being reached, no further increase in entropy is possible."

We know that heat, from the kinetic molecular point of view, is represented by the kinetic energy of the molecules of a system, the molecules moving about in a completely chaotic manner as a result of collisions. Owing to collisions any ordered arrangement which the molecules might be conceived of as possessing initially would be quickly annulled, and completely disordered distribution, both as to position and to molecular velocities, would ensue. This represents the direction of change in any spontaneous or naturally occurring process. That is, from the molecular standpoint a system always changes from an ordered to a chaotic state, and the change will go on until the molecular motion has become as disordered as possible. When this stage is reached, there is no longer any reason for further change. When equilibrium is reached the system has at the same time reached a maximum disorder or "mixed-up-ness". This involves the idea that a system in equilibrium possesses a maximum value of the probability of the state, the probability here referred to dealing with possible modes of molecular arrangement and velocity. We may call this the thermodynamic probability.

According to Boltzmann the thermodynamic probability of an ideal monatomic gas is a number which denotes by how many times or by how much the actual state of a gas system is more probable than a state of the same gas system (*i.e.* possessing the same total energy and volume) in which the molecules are equally spaced and all possess the same velocity. This "standard" state represents perfect order or arrangement of the molecules. It is of course never realised in practice owing to the disorder brought about as a result of collisions. The standard state represents the stage farthest away from the equilibrium state finally attained by the gas, in which final state the system is

completely chaotic. The probability of disorder is very much greater than the probability of complete order.

The thermodynamic probability of this "standard" state (that is the probability of complete order) is taken to be unity. It follows therefore that the thermodynamic probability of a real equilibrium state is an integral number usually much greater than unity. Thermodynamic probability differs therefore from mathematical probability in that the latter is always a fractional quantity, *i.e.* it denotes the ratio of the number of favourable cases to the total number of possible cases. Thermodynamic probability is proportional to but is not identical with mathematical probability.

It has just been stated that a system in equilibrium possesses a distribution or arrangement which is characterised by a maximum value for the thermodynamical probability of the state. It is necessary before going further to give a somewhat more concrete idea of what we mean by states or arrangements and the probability of arrangements. Let us leave the problem of molecules and turn to a very simple kind of system which can undergo various arrangements.

Let us suppose that we have two squares or areas denoted by the symbols I and II, and further let us suppose that we have five letters, *a*, *b*, *c*, *d*, *e*, and we wish to distribute or arrange these letters between the squares in every possible way. It is evident that all possible ways are included in the following :—

	I.	II.	Nature of Arrangement.
First arrangement :—			
1st *way* of arranging the letters is	abcde	—	All letters in I none in II.
Second arrangement :—			
2nd *way* of arranging the letters is	abcd	e	Four letters in square I ; one letter in II. There are five ways of producing this arrangement or distribution.
3rd " " " "	abce	d	
4th " " " "	abde	c	
5th " " " "	acde	b	
6th " " " "	bcde	a	
Third arrangement :—			
7th *way* of arranging the letters is	abc	de	Three letters in square I ; two letters in square II. There are ten ways of producing this arrangement or distribution.
8th " " " "	abd	ce	
9th " " " "	acd	be	
10th " " " "	bcd	ae	
11th " " " "	abe	cd	
12th " " " "	ace	bd	
13th " " " "	bce	ad	
14th " " " "	ade	bc	
15th " " " "	bde	ac	
16th " " " "	cde	ab	

We now begin with an arrangement similar to the first, but place all the five letters in square II and none in square I. Similarly we

can interchange squares I and II in the other two arrangements, so that in all, there are six *arrangements* possible in this system, and in all, thirty-two different *ways* in which these six arrangements or distributions may be carried out. Each of these *ways* is analogous to a "complexion" on Boltzmann's nomenclature. Every way or complexion is to be regarded as equally probable. It is very necessary to distinguish between arrangement or distribution and complexion. Thus in the first case, the arrangement is five letters in square I, none in square II. There is only one way or complexion of doing this. In the second arrangement, which consists of four letters in square I and one letter in square II, there are five ways or complexions of doing this. It is simply a question of combinations. Thus there are five letters to be divided in such a way that four are in one square, one in another square. The number of possible ways of doing this particular distribution is $\frac{\lfloor 5}{\lfloor 4 \ \lfloor 1} = 5$. In the third arrangement or distribution we have to distribute the letters so that there are always three in square I and two in square II. There are ten ways or complexions corresponding to this single distribution. This number is given by $\frac{\lfloor 5}{\lfloor 3 \ \lfloor 2} = 10$. Note that the problem is not *which* letters are in the squares, but how *many* different ways can they bed ivided to correspond with any particular arrangement, such as three letters in one square, two in the other.

If instead of five letters we had N letters and divided them between two squares, in such a way that n letters are in square I and N-n letters in square II, the possible ways or complexions possible to this particular distribution are—

$$\frac{\lfloor N}{\lfloor N - n \ \lfloor n}.$$

If, instead of two squares, we had m squares, the total number of complexions in a particular distribution would be given by—

$$\frac{\lfloor N}{\lfloor n_1 \ \lfloor n_2 \ \lfloor n_3 \cdot \cdot \cdot \ \lfloor n_m}$$

where $n_1 + n_2 + n_3 + \cdot \cdot \cdot n_m = N$.

To return to the simple case of five letters and two spaces. We have seen that there are *six* possible arrangement or distributions, *viz.* (5) (0); (4) (1); (3) (2); (0) (5); (1) (4); (2) (3). Each of these arrangements has its own number of ways or complexions. Thus for arrangement (5) (0), the number of complexions is one. For arrangement (4) (1), the number of complexions is five; for arrangement (3) (2), the number of complexions is ten. Similar numbers of complexions are found in the remaining arrangements or distributions.

It is evident that the arrangement (3) (2) has the same number of complexions as the arrangement (2) (3), and that either of these two arrangements or distributions possesses the *maximum number* of complexions. But the number of complexions is identical with the thermodynamic probability of the particular distribution under consideration. Either of the systems (3) (2) or (2) (3) possesses the *maximum probability*. Either distribution represents therefore the equilibrium distribution. The distribution (3) (2) or (2) (3) is the most likely distribution of five letters scattered at random between two squares. The equilibrium distribution in the above system is ten times more likely than the distribution (5) (0) or the distribution (0) (5), for the latter only possesses one complexion whilst the equilibrium distribution possesses ten.

The choice of five letters has somewhat obscured an important point in that we are led to two distributions of equal maximum probability. To find a closer analogue to the actual case of molecular systems containing an enormous number of molecules it is better to choose as the simplest model the distributions of six letters between two squares. With this system we have the following distributions and corresponding complexion-number for each distribution :—

			Complexion-Number.
1st distribution or arrangement	6 letters in I	0 letters in II	1
2nd " "	5 " "	1 " "	6
3rd " "	4 " "	2 " "	15
4th " "	3 " "	3 " "	20
5th " "	2 " "	4 " "	15
6th " "	1 " "	5 " "	6
7th " "	0 " "	6 " "	1
		Total number of complexions = 64	

The single arrangement or distribution which contains the maximum number of complexions is that represented by three letters in each square. This distribution has therefore the maximum probability, *i.e.* it is the one most likely to occur if six letters be scattered at random over two squares. This distribution is consequently the "equilibrium" distribution of the constituents of this system which consists of six letters.

Now let us apply this idea to a system of molecules. In this case also that distribution or arrangement which has the greatest number of complexions or ways is the most probable arrangement, its degree of probability, or simply its probability, being measured numerically by the number of complexions possible to it. The most probable distribution is the equilibrium distribution or state or condition of the system. A system changes in the sense that it tends to approach and finally reach an equilibrium state. In this state the number of possible

complexions is a maximum, *i.e.* greater than the number of complexions in any other distribution of the constituents of the system. A maximum number of complexions is identical with the idea of maximum disorder or maximum molecular chaos.

In all spontaneous processes the thermodynamical probability tends to reach a maximum. But on purely thermodynamical grounds we know that in spontaneous processes the entropy of a system tends towards a maximum value consistent with the total energy of the system. It follows therefore that there must be some close relation between the thermodynamical probability of a state and the entropy of the state. We can express this by writing—

$$S = F(w),$$

where S is the entropy of the system in any state, not necessarily the equilibrium state, w the thermodynamic probability of the same state, and F is some function still to be determined. To determine the nature of F, let us suppose that we have two independent systems, each one in a definite state, the entropy of the first being denoted by S_1, the probability of the state or arrangement of the first system being w_1, the entropy of the second system being S_2, and the probability of the state of the second system being w_2. We then have the relations—

$$S_1 = F(w_1)$$
$$S_2 = F(w_2).$$

The total entropy S of the two systems taken together is the sum of the separate entropies. That is—

$$S = S_1 + S_2 = F(w_1) + F(w_2).$$

Since the particular state or arrangement of the first system can be realised by selecting any *one* of the w_1 complexions (contained in or characteristic of that arrangement or state) and similarly for the second system, it follows that the state or arrangement of the combined system can be realised by selecting any one of the w_1 complexions of the first and combining them with the w_2 complexions of the second. That is, the compound arrangement is obtained by selecting any one of the w_1 and w_2 complexions. That is the probability w of the compound state is $w_1 \times w_2$.

But for the compound system we have the relation: $S = F(w)$. Hence from the above we get: $S = F(w_1 \cdot w_2)$. But we have already seen that $S = F(w_1) + F(w_2)$. Hence, $F(w_1 \cdot w_2) = F(w_1) + F(w_2)$.

The only function which will satisfy this relation is the logarithmic one, *i.e.* $\log xy = \log x + \log y$.

Hence, the connection between the thermodynamic probability and the entropy of a system is given by the relation:—

$$\text{Entropy} \propto \log_e \text{Probability}$$

or

$$S = k \log_e W,$$

where k is a constant independent of the chemical nature of the system

and independent of the conditions under which the system is examined. A more general form of the above expression is—

$$S = k \log W + \text{constant}.$$

We have now to find out the significance of the universal constant k.

To do this we make use of a statistical expression arrived at by Boltzmann for the entropy of a perfect monatomic gas. A monatomic gas is one in which the total or internal energy U is due entirely to the kinetic energy of the molecules. Boltzmann's expression is—

$$S = 3/2kN \log U + kN \log v + K$$

where U and k are defined above, N is the number of molecules in the system, v the volume of the system, and K is a constant independent of the energy and volume but involving the number and mass of the molecules. It has already been shown in Volume II. that the following purely thermodynamical relation holds good :—

$$\frac{\partial S}{\partial T} = \frac{I}{T}\frac{\partial U}{\partial T}.$$

Differentiating Boltzmann's expression for the entropy of a perfect monatomic gas we obtain :—

$$\frac{\partial S}{\partial T} = 3/2kN\frac{I}{U}\cdot\frac{\partial U}{\partial T}.$$

Hence $U = 3/2kNT$.

If N be taken as denoting the number of molecules in one gram-molecule, then U denotes the total energy of one gram-molecule of monatomic gas.

But we have already seen (Vol. I.) that in the case of a perfect gas, the total *kinetic* energy of all the molecules forming one gram-molecule is $3/2RT$, where R is the gas constant per gram-molecule. Further in the case of a monatomic gas the internal energy is entirely kinetic. Hence for one gram-molecule of a monatomic gas: $U = 3/2RT$.

It follows therefore that—

$$Nk = R,$$

or *k is the gas constant per single molecule.*

Further, in the case of a perfect gas, $3/2R = C_v$ where C_v is the gram-molecular heat at constant volume. Hence the equation of Boltzmann for the monatomic gas becomes—

$$S = C_v \log T + R \log v + K_1$$

where S now denotes the entropy of one gram-molecule. This expression is in complete agreement with that already deduced in Volume II. on thermodynamical grounds, *viz.* :—

$$S = C_v \log T + R \log v + S_1$$

if we identify S_1 with K_1. This constant represents the value of the entropy under certain conditions. On purely thermodynamical grounds

it is legitimate to consider that the entropy may assume in general any value whatsoever, positive or negative, and that therefore all that we can measure is the *change* in entropy resulting from a physical or chemical process. It will be pointed out later in dealing with Nernst's Heat Theorem, that according to Planck, the Heat Theorem itself is equivalent to regarding the entropy of all substances as zero at the absolute zero of temperature, and possessing therefore a positive value at all other temperatures.[1] This gives us a starting point from which to calculate not only change in entropy but its absolute value under given conditions. This likewise agrees with the simplified expression: $S = k \log W$ in which W has been defined as a quantity greater than unity, and consequently S is essentially positive. Of course if we retain the constant in the expression: $S = k \log W +$ constant, the value of S may be positive or negative depending upon the magnitude and sign of the integration constant whether W itself is greater than unity or not. Classical statistical mechanics, which did not attempt to assign any particular limit to the value of the entropy, is represented by the above expression. If we assume with Planck that the integration constant is zero, and remembering that W as defined above is greater than unity, it follows that S is a positive term becoming zero at absolute zero. This is equivalent to assuming the quantum hypothesis.

The general position which we have now reached as a result of the considerations dealt with in this section may be summarised as follows:—

The second law of thermodynamics, regarded as a law of experience, states that, whilst work may always be completely converted into heat, heat on the other hand cannot be completely converted into work. In other words, all natural spontaneous processes are thermodynamically irreversible. In mechanics we deal only with reversible processes, and from the standpoint of mechanics alone we would expect heat to be as readily convertible into work as work into heat. Since this is not the case there must be something characteristic of molecular systems to which the irreversibility is due. This "something" is discovered in the fact that heat consists of a chaotic motion of the molecules, and that as a result of collisions this motion tends to become as chaotic or disordered as possible. In other words, the irreversibility which finds expression in the second law of thermodynamics is due essentially to the fact that ordered motion always tends, of its own accord, to become disordered, and chaotic motion never tends, of its own accord, to become ordered.

This statement is a statement of the second law of thermodynamics not expressed simply as a result of experience but in terms of statistical mechanics. We have therefore found a mechanical basis for the second law.

It is obvious at the same time why Gibbs gave the significance

[1] According to Planck this assumption is "the very quintessence of the hypothesis of quanta". It must be pointed out that whilst this assumption makes the theory of quanta and Nernst's Heat Theorem *agree*, it is not essential to the deduction of the heat theorem itself, which only requires that the entropy of all substances at absolute zero shall be the *same*, but not necessarily zero.

"mixed-up-ness" to the concept of entropy; for maximum mixed-up-ness means on the mechanical view maximum stability or equilibrium, and hence when equilibrium exists the entropy is a maximum. The same idea is involved in the term "run-down-ness" employed by Tolman as a descriptive mechanical term for entropy. The latter term appeals to the mind as being particularly applicable to a chemical reaction which proceeds in order to attain an equilibrium state at which the system will, chemically speaking, have completely "run down".

The Principle of Equipartition of Kinetic Energy.

This principle, which has been deduced on the basis of statistical mechanics by Maxwell and by Boltzmann (*cf.* Jeans, *Dynamical Theory of Gases*), has already been employed in Chap. I. of Vol. I. in dealing with Perrin's method of determining the Avogadro Constant from measurements made upon emulsions. The principle states that in a system consisting of a large number of particles (*e.g.* molecules) the kinetic energy is on the average equally distributed amongst the various degrees of freedom possessed by these particles. The first point with which we have to deal is the term *degree of freedom*.

A degree of freedom is represented by a co-ordinate. We may take the term as meaning an independent mode in which a body may be displaced or a possible mode or direction of motion. We shall consider briefly the problem of the number of degrees of freedom possessed by bodies in the gaseous and solid states of matter respectively. First of all a word about energy in general. We are familiar with the two kinds of energy which material systems may possess, namely, kinetic and potential. These "kinds" of energy are not to be confused with the "types" of energy of which we are about to speak. A "type" may consist of kinetic and potential energy together, or simply kinetic alone. A gas molecule can possess theoretically three *types* of energy, each of which is a function of the temperature: (1) *Energy of Translation;* (2) *Energy of Vibration*, and (3) *Energy of Rotation.*

1. *Energy of Translation.*—This type of energy is possessed in virtue of the free translational motion of the molecules along free paths throughout the whole of the system. The energy in this case is entirely kinetic. It has been represented diagrammatically in Chap. I. of Vol. I. in connection with Perrin's work on Brownian movement. Every gas molecule possesses translational motion and consequently translational energy. Since the direction of any movement of this kind can be represented by the three space co-ordinates, we conclude that translational energy corresponds to three degrees of freedom. The energy of translation is the same for any moving molecule at a given temperature. Further, such a molecule possesses just three degrees of freedom in respect of translation whether the molecule be monatomic or polyatomic; the constitution of a molecule does not enter into the question of its translational energy.

2. *Energy of Vibration.*—This type of energy exists in virtue of the

oscillations of particles with respect to a fixed centre of gravity. Vibration is only possible when there is a restoring force acting upon the particle which tends to make it take up a mean position. The existence of the restoring force is the factor which distinguishes vibration from translation and also from rotation to be mentioned later. We meet with vibration in the case of the atoms inside a molecule of a gas, and likewise in the case of the atoms composing a solid. Vibration is always a constrained movement. We can conceive of vibration as corresponding either to one or to two or to three degrees of freedom. When we speak of vibration in connection with molecules it is always to be understood that we are referring to the vibrations of the *atoms* inside the molecule. One such atom can vibrate with respect to the other in the case of a diatomic molecule. In this case the vibration is linear, that is, it is along the line joining the two atom centres. Since the vibration is linear there is one degree of freedom in this case. Linear vibration is represented in diagram (*a*) Fig. 2.

FIG. 2 (*a*).—*Linear vibration* of atoms in a diatomic molecule. One degree of freedom. Energy, kinetic + potential.

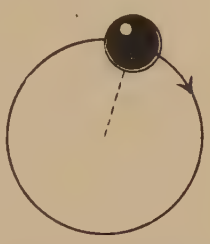

FIG. 2 (*b*). — *Circular vibration* or *spin* of an atom round a centre of gravity. Two degrees of freedom. Energy, kinetic + potential.

It is also conceivable that the vibration of the particle, an atom or an electron, may be circular. That is, the particle may describe a circular path about a centre of gravity, the orbit being traced out on a surface. Hence in such a case there are two degrees of freedom to be attributed to the vibration. This is represented by the spinning motion shown in diagrams (*b*) and (*c*), Fig. 2. Further, in the case of a monatomic solid (such as a metal) the only type of motion which can be ascribed to the atom is vibration. Free translation cannot exist, for if it did the solid would not retain its crystalline form. In this case the vibration of every atom can take place in three directions in space with respect to the centre of gravity or mean position of the atom. There are therefore three degrees of freedom to be attributed to the vibrations of the ultimate particles in a solid. This is represented in diagram (*d*), Fig. 2. The characteristic feature of all vibrations is the existence of potential as well as kinetic energy. As will be shown later

each complete vibration on the average contains just as much potential energy as it does kinetic.

To return to the vibrations of the atoms in a gas molecule. In the case of a diatomic molecule the molecule is said to possess one degree of freedom in respect to the to-and-fro vibration of one atom with respect to the other. The molecule also possesses three degrees of freedom in respect of translation of the molecule as a whole. In a triatomic molecule the atoms ABC probably vibrate in pairs, AB, BC, CA, each pair functioning like a diatomic molecule, so that the molecule as a whole has three degrees of freedom in respect of atomic vibrations. The molecule possesses in addition three degrees of freedom in respect of translation. Hence, in the case of a triatomic molecule there are three degrees of freedom in respect of translation and three in respect of vibration.

It is obvious that no atomic *vibration* is possible in the case of a monatomic molecule in a *gas*. If such an atom is displaced there is no restoring force; the atom is not connected to any other as in the case

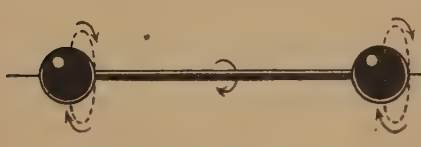

FIG. 2 (*c*).—"Spinning molecule." Two degrees of freedom. Energy, kinetic + potential. (Motion *not* maintained by collisions.)

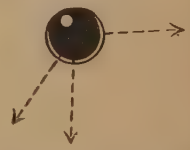

FIG. 2 (*d*).—*Trilinear vibration* of an atom in a solid. Three degrees of freedom. Energy, kinetic + potential.

of diatomic molecules, and any displacement would simply be identical with free translation. Contrast this with the behaviour of monatomic molecules in solids in which any displacement can only take place against a restoring force, with the result, as already mentioned, that the vibration in the case of a solid possesses three degrees of freedom. In the case of a monatomic gas vibration is impossible, and, so far as we have gone, we can only ascribe to this kind of molecule energy of the translational kind. A difficulty crops up when we come to consider a monatomic gas molecule in the light of the third possible type of motion, *viz.* molecular rotation.

The circular vibration represented by diagram (*c*), Fig. 2, requires a little more consideration. The amount of energy represented by a circular vibration or spin depends upon the square of the rate of spin and upon the moment of inertia of the spinning particle.[1] If a di-

[1] If a particle of mass m moving in a circle of radius r round a fixed position with an angular velocity ω (ω being the number of radians swept out by the particle per second), then the speed of the particle is ωr and its kinetic energy $E = 1/2\, m \cdot \omega^2 r^2$. This expression can also be written: $E = I \cdot 1/2 \cdot \omega^2$, where $I = mr^2$. The quantity I is called the moment of inertia of the particle. The dimensions of

atomic molecule were really represented by the diagram (*c*), Fig. 2, *i.e.* if the atoms were massive spheres extending a sensible distance from the axis, the energy of the motion represented in the diagram would be sufficiently large to make its presence felt in the molecular heat of the gas. As a matter of fact this type of circular vibration does not affect the molecular heat sensibly. This arises from the now accepted conclusion that practically the entire mass of any atom is concentrated in a nucleus situated at the centre of the atom, the dimensions of the nucleus being small even compared with those of the atom (*cf.* Chap. V., the Rutherford-Bohr atomic model). Hence, in the motion represented in diagram (*c*), Fig. 2, the mass of the two atoms, *i.e.* the mass of the whole molecule is practically all concentrated *upon* the axis of circular vibration (the figure axis in this case), and the moment of inertia of the atoms, and consequently the energy in respect of this motion is negligible, because the r term referred to in the footnote is practically zero. Further, as shown in Chap. V., each molecule possesses a number of electrons likewise spinning, as in diagram (*c*), Fig. 2. In the case of the electrons the distance r is not negligible, but on the other hand the mass of the electron is so small a fraction of the total mass of the molecule that again the moment of inertia is small and the energy of electronic spin does not enter sensibly into the "ordinary" energy content of the molecule, the variation of which (energy) with temperature is given by the molecular heat. The molecular heat term is due to energy of translation, of linear vibration and of molecular rotation or its equivalent, precessional vibration (*cf. infra*). The electron spin enters into the question of the ultra-violet spectrum of the gas, *cf.* Chap. V. It must be assumed, of course, that such a spin as that represented in the diagram (*c*), Fig. 2, takes place in all cases. It is scarcely affected by temperature, however, and consequently does not enter into molecular heat values, except in the limit when the temperature is very high.

3. *Energy of Molecular Rotation.*—If a molecule resemble a solid sphere we would expect it to rotate in the manner indicated in Fig. 3, diagram (*a*). The rotation of a sphere can be referred to three axes of rotation, *i.e.* there are three degrees of freedom. The energy is entirely kinetic. Molecules, however, are not necessarily spherical unless they contain a number of atoms. It is believed that at least three atoms must be present in a molecule before we can possibly ascribe to the molecule as a whole the limiting number (3) of degrees of freedom in respect of rotation.

It is a remarkable fact that monatomic gas molecules do not appear to possess rotational energy. This conclusion rests upon the experimental fact that the molecular heat of argon and other monatomic gases and metallic vapours can be accounted for by simply assuming *translational* energy. This point will be dealt with later. A monatomic

the particle in the above case are supposed to be small compared with r. In the case of a solid sphere the moment of inertia of the sphere can be shown to be $2/5 \cdot M \cdot r^2$, the axis of rotation passing through the centre of the sphere.

gas molecule appears to function simply as a massive point, and not as a massive sphere. This is a remarkable conclusion. It is self-evident that *vibration* of the atom cannot occur in the case of a mon-

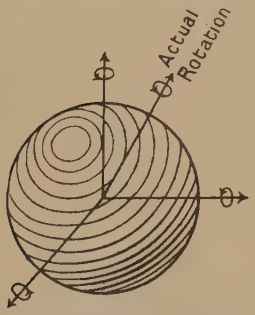

FIG. 3 (*a*).—Sphere with three component rotations. Three degrees of freedom. Energy, kinetic.

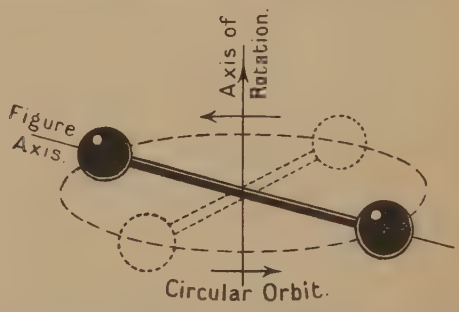

FIG. 3 (*b*).—*Molecular rotation of diatomic molecule* (due to collisions). Two degrees of freedom. Energy, kinetic.

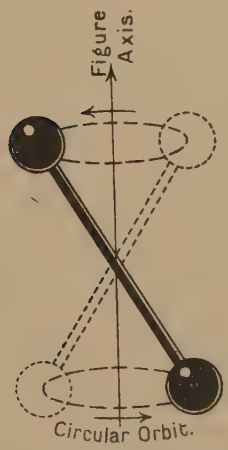

FIG. 3 (*c*).—*Precessional vibration* (due to collisions). The molecule possesses gyroscopic properties. Two degrees of freedom. Energy, kinetic.

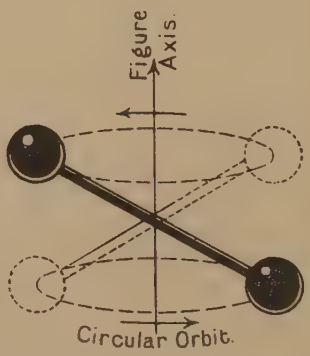

FIG. 3 (*d*).—*Extreme precessional vibration* (due to collisions at high temperatures). Merging into ordinary molecular rotation.

atomic molecule. It is by no means clear why *rotation* of the monatomic molecule as a whole apparently does not occur. It is possible that rotation is actually occurring but that the energy term corresponding thereto is negligibly small for the same reasons as those advanced in

considering the circular vibration of diagram (*c*), Fig. 2. This point has not yet been settled.

Molecular rotations are ascribed to collisions with other molecules. This distinguishes molecular rotation from atomic vibration as far as origin is concerned. Atomic vibration can indeed be affected by collisions, but the origin of atomic vibration is more deeply seated, so to speak, than that of molecular rotations. Presumably atomic vibration is set up as a result of absorption of radiant energy on the part of the molecule. This might occur at a collision, but not necessarily so; unless the collision be very inelastic (*cf.* Chap. VI., the section dealing with resonance and ionisation potentials).

When a molecule consists of more than one atom it seems reasonable at first sight to ascribe to the *molecule as a whole* a certain amount of rotational energy. The reason for the qualifying clause will not be given now; the point is taken up in Chap. IV. in connection with the theory of the molecular heats of gases. As Krüger has shown, in place of true molecular rotations we may have to substitute another kind of motion, namely, *precessional vibrations.*[1] The possible kinds of rotations and precessional vibrations in the case of a diatomic molecule are illustrated in Fig. 3, diagrams (*b*) to (*d*). It must be understood that rotation *or* precessional vibration always refers to the molecule as a whole. This is in contrast with the view taken of true *atomic* vibrations which have been discussed.

As regards the rotation of a diatomic molecule the diagram (*b*), Fig. 3, shows us that there are two degrees of freedom, *i.e.* there are two co-ordinates at right angles defining the surface over which the rotation of such a molecule can take place. The axis of rotation is at right angles to the plane indicated in the diagram.

From the point of view of the internal molecular energy the significance of the rotation of the molecule depends upon its moment of inertia, *i.e.* the moment of inertia of each of the atoms with respect to the axis of rotation and the number of revolutions ν which the molecule makes per second (as a result of collisions). The rotational energy is given by the expression $1/2 \cdot I \cdot (2\pi\nu)^2$, where I is the moment of inertia and ν has already been defined.

[1] The term "precessional vibration" requires perhaps a word of explanation. The type of motion represented by the term is shown in diagrams (*c*) and (*d*), Fig. 3. It is similar to the true precession of a gyroscope, but with this difference that a diatomic gas molecule does not precess in a definite field of force. It is assumed, in fact, that there is no field of force. Precessional vibration (which must not be confused with nutation) is brought about in the case considered by the collisions of molecules with one another, each molecule being assumed to possess gyroscopic properties in virtue of the electrons which it contains, and which spin [circular vibration] around the figure axis as already indicated in diagram (*c*), Fig. 2. If no collision occurred a diatomic molecule would spin with a fixed axis. As a result of collision the spin is disturbed and the figure axis itself describes the circular motion represented in diagram (*c*), Fig. 3. It maintains this type until a further collision occurs which sets up a new vibrational precession, the figure axis now precessing round a circle which has a greater or less circumference than before. Such precessional vibrations might be more accurately described as Poinsot movement, dealt with in rigid dynamics. The introduction of the idea into molecular motion and molecular heat is due to Krüger, *cf.* Chap. IV.

In the case of a diatomic molecule we have therefore three degrees of freedom in respect of translation, one degree of freedom in respect of linear vibration of the atoms, and two degrees of freedom in respect of molecular rotation; six degrees in all. If we regard rotation as impossible we have to substitute precessional vibration of the molecule which corresponds to two degrees of freedom; again six degrees of freedom in all.

In the case of a molecule containing more than two atoms, if rotation be possible at all, it is reasonable to ascribe three degrees of freedom in respect of such rotation, *i.e.* the limiting number of degrees of freedom. At the same time the molecule possesses three degrees of freedom in respect of translation and three degrees of freedom in respect of atomic vibrations in pairs; in all nine degrees of freedom. In the case of translation and of rotation[1] the energy is entirely kinetic; in the case of vibration it is potential as well as kinetic. The possible degrees of freedom in various kinds of gas molecule are summarised in the following table which is due to Bjerrum (*Zeitsch. Elektrochem.*, **17**, 731, 1911); the general correctness of the assigned values is borne out to a certain extent by the values of the molecular heats of the respective gases:—

No. of Atoms in the Molecule.	Number of Degrees of Freedom.		
	In Virtue of Translation.	In Virtue of Rotation.	In Virtue of Vibration.
1	3	0	0
2	3	2	1
3	3	3	3
4	3	3	6

Our knowledge of the *liquid state* is so scanty that it has not been possible hitherto to assign any definite value to possible number of degrees of freedom. A liquid molecule must, of course, possess three degrees of freedom in respect of translation; it must likewise possess

[1] In regarding the rotation of a diatomic molecule as representing kinetic energy alone, we are assuming that the bond between the atoms is quite firm. In general, however, we may expect a certain amount of "give" due to the atoms being "centrifuged" from one another in the rotation. If this occurs it will involve a certain amount of potential energy. Bjerrum (*loc. cit.*) finds that the kinetic energy E_K of molecular rotation is related to the potential energy E_P by the equation—

$$E_p/E_k = RT/4\pi^2\nu^2Mr^2$$

where ν is the frequency of internal vibration, M is the mass, and r the radius of the molecule. Taking the case of oxygen at ordinary temperatures where $\nu = 10^{14}$, $r = 10^{-8}$, and $M = 32$, it is found that—

$$E_p/E_k = 0{\cdot}00002.$$

That is, the potential energy of rotation is negligible compared with the kinetic energy.

an unknown number in respect of rotation and vibration. We pass on, therefore, to the *solid state*. In the case of a solid, *i.e.* a crystalline substance, and probably also in the case of a super-cooled liquid like glass, it is necessary to regard translational energy (and also rotational energy) as absent, the energy possessed by the molecules of a solid being vibrational. As already stated, vibration of each atom can take place along all *three* axes, so that even the simplest type of solid possesses three degrees of freedom. We shall return to this later.

For the present we have to take up the application of the principle of equipartition of (kinetic) energy amongst degrees of freedom. According to this principle, when a system is in *statistical equilibrium*, such equilibrium being determined by a number of variables, *i.e.* degrees of freedom, to each such variable *one must attribute the same quantity of* (*kinetic*) *energy*. It is to be remembered that there is no restriction as regards the physical state of the system—the principles applies equally well to gaseous, liquid, or solid systems and to systems embracing two or more such states simultaneously. It is supposed to hold equally well also for degrees of freedom in respect of translation, vibration, or rotation. To see how much this energy amounts to per degree of freedom, let us consider the kinetic energy of translation of a perfect gas at a given temperature. First of all we have the relation—

$$PV = RT.$$

Further, we have seen in the theoretical deduction of Boyle's Law that—

$$P = \tfrac{1}{3}\rho u^2$$

where ρ is the density of the gas and u the root-mean-square velocity. If we are considering 1 gram-molecule of the gas, $\rho = \dfrac{\text{molecular weight (M)}}{V}$, where V is the molecular volume, and hence we can write—

$$PV = \tfrac{1}{3}Mu^2 = \tfrac{1}{3}Nmu^2$$

where m is the mass of a single molecule and N the number of molecules in 1 gram-mole. Taking into the consideration the first equation, we obtain—

$$RT = \tfrac{1}{3}Mu^2 = \tfrac{1}{3}Nmu^2.$$

Now the kinetic energy of a single molecule is $\frac{1}{2}mu^2$, and hence the kinetic energy of 1 gram-mole is $\frac{1}{2}Nmu^2$. That is the kinetic energy of 1 gram-mole is $\frac{3}{2}RT$, and this holds good whether the gas be monatomic or polyatomic. Now a gas molecule has three degrees of freedom in virtue of translation, and hence by applying the equipartition principle, EACH DEGREE OF FREEDOM POSSESSES KINETIC ENERGY EQUAL TO $\frac{1}{2}RT$.

This is the quantitative form of the principle of equipartition of energy between degrees of freedom. The principle does not mean that in a gas system, for example, the kinetic energy of translation of every

molecule shall be exactly $3/2kT$, where k is the gas constant per single molecule. We know from Maxwell's distribution law that the kinetic energy varies in general from molecule to molecule. What the equipartition principle does mean is that on the average the kinetic energy of a molecule is $3/2kT$.

Let us now consider the special case of a monatomic gas. As we have already seen, it can possess no vibrational energy: whether it possesses rotational energy is at this stage a doubtful point. Its energy, due to translational motion, for 1 gram-mole at T° abs. is $\frac{3}{2}RT$, when R = 1·985 cals. Now the specific heat C_v at constant volume is simply the increase in the *total* energy per degree. If we are dealing with 1 gram-mole or gram atom as unit of mass, the heat term will be the so-called molecular or atomic heat C_v. It is clear from definition that the increase in the

(kinetic) energy of translation[1] per 1° rise in temperature $= \frac{\partial}{\partial T}(\frac{3}{2}RT)$

$= \frac{3}{2}R = 2{\cdot}98$ cals. per mole. Recent experiments of Pier in Nernst's Laboratory (*Zeitsch. Elektrochem.*, **15**, 546, 1909; **16**, 897, 1910) have shown that the molecular heat of argon is 2·98 cals. per mole, and further that this is *independent* of temperature. This agreement suggests that one should neglect the rotational energy of the monatomic molecule (vibration of atoms inside the molecule is naturally impossible since the gas is monatomic). In fact the monatomic molecule seems to function as a massive point. Agreement of this order between calculated and experimental values is, however, not found in other cases. Thus, taking the case of a *diatomic* gas, the number of degrees of freedom in virtue of translation is again 3. The number of degrees of freedom in virtue of vibration we have considered as 1; that is 4 degrees in virtue of translation and vibration. The corresponding kinetic energy of such a molecule will be $4 \times \frac{1}{2}RT = 4{\cdot}0\ T$ cal./mole, if the law of equipartition be assumed. Of course this does not represent all the energy due to translation and vibration. In vibrations we have potential energy as well as kinetic which must be taken account of. It can be shown by a simple calculation that the potential energy of a particle undergoing what we might call "circular vibration" is just *equal* to the kinetic energy of the vibration. The calculation is as follows:—

Consider a particle whose mass is m travelling in a circle round a centre of gravity with velocity u. Suppose r is the radius of the circular path. A motion of this kind involves the action of two opposing forces, one tending to draw the particle towards the centre, its position of rest, the other due to the motion of the particle tending to make it fly off at a tangent. The two forces must just balance in order to make the circular movement permanent. Let us suppose that the diameter of the circle, *i.e.* the amplitude of the vibration, to be so small that the force tending to draw the particle back to the centre is proportional to the distance of the particle from the centre. This very simple law of

[1] Energy of translation is necessarily entirely kinetic, and it is to the distribution of *kinetic* energy amongst degrees of freedom that the law of equipartition is properly to be applied.

attraction can only hold when the particle is not far removed from the centre, *i.e.* when r is small. If A is this attractive force per unit distance from the centre, then on the assumption just made, the force acting inwards at a distance r is Ar. We have now to calculate this force in terms of the motion of the particle. Consider the particle traversing the circular path shown in the figure (Fig. 4).

Suppose that the particle is at the point a, travelling with a velocity u in the direction aT. After a short interval of time δt it is at b travelling with a velocity u in the direction Tb. The arc $ab = u\delta t$, and so the radian measure of the angle aob or cTd is $\delta\theta = u\delta t/r$. If $Tc = Td = u$, then the velocity has changed from one represented in magnitude and direction by Tc to one represented by Td. By the triangle of velocities, the change in velocity is represented in magnitude and direction by the line cd. The direction of cd is the same as that of TO; and its magnitude is $2u \sin \delta\theta/2$. In the limit when δt is infinitesimally small $\sin \delta\theta/2 = \delta\theta/2$, or the change of velocity is $u\delta\theta$, *i.e.*, $u^2\delta t/r$.

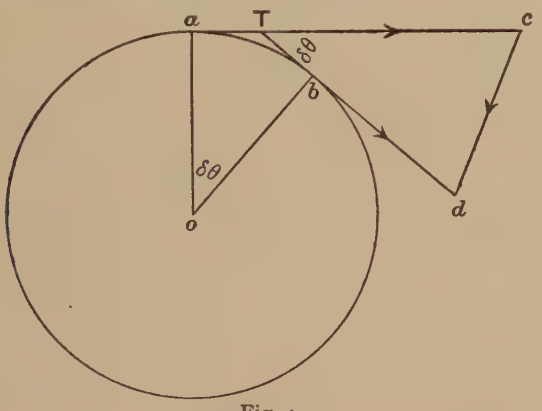

Fig. 4.

Hence the acceleration inward (*viz.* the velocity inward divided by δt is equal to u^2/r. But force = mass × acceleration. Hence the force acting inwards and preventing the particle from flying off is mu^2/r. This must be identical with Ar. That is—

$$mu^2/r = Ar.$$

Further, the potential energy of the particle at a (namely, the work which must be done upon the particle to bring it from the position of rest, the centre of the circle, to the point a on the circumference) is the product of the force acting into the distance traversed. The force varies at every stage of the radius, so that it is necessary to integrate the work expression for each increment dr in order to obtain an expression for the potential energy of the particle at the point a. That is the potential energy of the particle when it is on the circumference is $\int_0^r Ar\,dr$ which

is $\frac{Ar^2}{2}$. But it has just been shown that $Ar = mu^2/r$. Hence the potential energy, *viz.* $\frac{Ar^2}{2}$ is equal to $(1/2)mu^2$. But the term $(1/2)mu^2$ is the average *kinetic* energy of the particle. Hence in a complete circular vibration *the kinetic energy is just equal in magnitude to the potential energy.*

We return now to the question of the diatomic molecule.

The linear vibration executed by one atom with respect to the other involves one degree of freedom, *i.e.* the line of junction of the two atoms. On the equipartition principle the kinetic energy involved per mole is $\frac{1}{2}RT$. Since there is likewise an equal amount of potential energy, the total energy due to vibration is $1RT$. Adding the amount due to the (kinetic) energy of translation of the diatomic molecule as a whole, *viz.* $\frac{3}{2}RT$, we obtain $\frac{5}{2}RT$ as the *total* energy due to translation and vibration. That is, the rise in this energy per 1° is $\frac{5}{2}R = 5{\cdot}0$ cal. per mole per degree, taking $R = 2$ cals. If now we take rotation of the molecule as a whole into account we again have two degrees of freedom, to which one must assign RT units of kinetic energy. The total energy of a diatomic molecule, provided the law of equipartition is true, and *provided* ALL *the degrees of freedom are effective*, should be $\frac{7}{2}RT$, and the molecular heat therefore $\frac{7}{2}R = 7{\cdot}0$ approx.

Experiment shows, however, very different values. For hydrogen at 0° C. the molecular heat $C_v = 4{\cdot}9$ to $5{\cdot}2$ cal. per degree, and at 2000° C., $C_v = 6{\cdot}5$ cal. (*cf.* Nernst, *Zeitsch. Elektrochem.*, **17**, 272, 1911). For nitrogen at 0° $C_v = 4{\cdot}84$, and at 2000° $C_v = 6{\cdot}7$. For chlorine at 0° $C_v = 5{\cdot}85$, at 1200° $C_v = 7{\cdot}0$. For oxygen at 0° $C_v = 4{\cdot}9$, at 2000° $C_v = 6{\cdot}7$. These values are only approximately correct. It is evident, however, that not only is there lack of agreement in the numerical values between those observed and those calculated at lower temperatures, but the fact that the *molecular heat of diatomic gases varies considerably with the temperature is quite unaccounted for by the theory of equipartition* unless, indeed, the number of degrees of freedom is a function of the temperature; which is difficult to believe.

In the case of triatomic gas molecules the degrees of freedom in respect of translation are three, the [kinetic] energy corresponding being $\frac{3}{2}RT$. As regards vibration, there are possibly three vibrating pairs each with one degree of freedom, corresponding to the quantity $3 \times \frac{1}{2}RT$ of *kinetic* energy. To this has to be added an equivalent amount of potential energy, making $3RT$ as the total energy term in respect of vibration. Hence translation and vibration apparently entail $\frac{9}{2}RT$ units of energy, and the increase in this for 1° rise in temperature is $\frac{9}{2}R = 9{\cdot}0$ cal. per mole per degree. Logically we should likewise add a term for rotation of the molecule as a whole, which we have seen amounts to $\frac{3}{2}RT$. The observed molecular heat C_v for CO_2 at 18° is $7{\cdot}09$, and this becomes $10{\cdot}47$ at 2210° (Pier, *l.c.*). For water vapour C_v at 50° C. = $5{\cdot}96$ (Nernst and Levy), and at 2327° C., $C_v = 9{\cdot}68$ (Pier). Again the discordance between theory and experiment is very apparent since theory predicts a *constant* molecular heat of either 9 or 12 cals. per mole per degree.

The Ratio γ for Gases, and the number of "effective" Degrees of Freedom.

It may easily be shown (*cf.* Meyer's *Kinetic Theory of Gases*, p. 140 *seq.*) that the ratio $\frac{C_p}{C_v}$ or γ can be expressed approximately in the form—

$$\gamma = 1 + \frac{2}{n}$$

where n is the number of degrees of freedom of the gas molecule. In the case of monatomic gases the value of γ is 1·666, and this is the quantity which is obtained on putting $n = 3$ in the above expression. That is, a monatomic gas molecule possesses three degrees of freedom, in respect of translation only. This agrees with the conclusion we came to above (though, of course, it must be remembered that the actual number of degrees is *possibly* greater than this, *i.e.* degrees in virtue of rotation, but for some unknown reason only some are effective in regard to heat capacity, for after all an atom is *not* a point in the mathematical sense). In the case of a diatomic molecule the value of γ, found by experiment, is in many cases 1·4, and this will correspond to putting $n = 5$ in the above equation. In triatomic gas molecules $\gamma = 1{\cdot}3$ in general, and this makes $n = 7$. These numbers are certainly less than the actual number of degrees of freedom possessed by di- and triatomic gases, as is indeed shown by the fact that there are some diatomic gases with as small a value as 1·29 for γ (iodine vapour) and some triatomic gases, *e.g.* CS_2, for which $\gamma = 1{\cdot}2$. *Further, the values of γ are not constant but vary with the temperature.* The whole problem of the number of degrees of freedom is, therefore, in a very unfinished state.

The doubt which exists, in the case of polyatomic molecules, regarding the true number of degrees of freedom, takes away from the force of the criticism levelled against the principle of the equipartition, on the ground of the lack of agreement between observed and calculated molecular heats. The soundest criticism of the principle rests on the experimental observation that the molecular heat *varies* with the temperature, whilst the principle leads us to expect it to be constant, no matter how many degrees of freedom be present.

Atomic Heat of Solids.

Since the equipartition principle is considered to hold equally well for all states of matter, the term $\frac{1}{2}RT$ must represent the *kinetic* energy per degree of freedom of 1 gram-mole of any system at the temperature T. In solid elements—the metals—it is generally agreed that the gram-molecule and gram-atom are identical, so that in such a case $\frac{1}{2}RT$ is the kinetic energy per degree of freedom for each gram-atom, R being put equal to 1·985 cals. The orientation of the atom of a metal is such, that it is free to vibrate in any direction which can be

resolved in terms of the three space co-ordinates X, Y, Z. Such a particle possesses three degrees of freedom [1] (*cf.* Fig. 2, diagram (*d*)).

The *kinetic* energy in virtue of this "space" vibration is evidently $\frac{3}{2}$RT, and since any vibration [2] involves an amount of potential energy equivalent to the kinetic, the total energy of 1 gram-atom of a monatomic solid is 3RT, according to the principle of equipartition of energy. Now the atomic heat C_v at constant volume is simply the change of total atomic energy per degree, that is—

$$C_v = \frac{d}{dT}(3RT) = 3R = 5{\cdot}955 \text{ cals.}$$

The application of the equipartition principle has therefore led to the conclusion that the atomic heat of monatomic solids should be a constant, viz. 5·955, *the same for all monatomic solids and independent of temperature* (the term 3R does not contain T; though, of course, the *total energy* present in the solid at any given temperature depends on this temperature, *viz.* 3RT in the above case). This result is practically identical with Dulong and Petit's experimentally discovered law, and this agreement is one of the most striking pieces of evidence in favour of the equipartition principle. The following table gives the values of atomic heats for a number of elements at 20° C. (*cf.* G. N. Lewis, *Journ. Amer. Chem. Soc.*, **29**, 1168, 1907):—

3R = 5·955.

Element.	Atomic Heat at Constant Volume.	Element.	Atomic Heat at Constant Volume.
Na	6·4	Cd	5·9
Mg	5·8	Sn	6·1
Al	5·6	Sb	5·9
K	6·5	I	6·0
Fe	5·9	Pt	5·9
Ni	5·9	Au	5·9
Cu	5·6	Tl	6·1
Zn	5·7	Pb	5·9
Pd	5·9	Bi	6·2
Ag	5·8		

The approximation of these values to that of 3R is obviously very close. Nevertheless, too great stress cannot be laid upon this, for *it has been shown by experiment that the atomic heat of solids* (*as in the case of gases*) *is a function of the temperature, decreasing to very small values at very low temperatures.* We shall take this question up later on in discussing the work of Einstein and of Nernst. Sufficient has been said,

[1] In the case of metals each atom vibrates independently of others, at least as long as its amplitude is less than the mean distance of the atoms apart, and hence three degrees of freedom must be ascribed to it.

[2] That is, any vibration of the simple harmonic kind, in which the restoring force is proportional to the distance from the centre.

however, in this connection to show that while the principle of equipartition is *partially* true, in the form given by Boltzmann it is not sufficiently comprehensive. It might be thought that a sufficient explanation of the observed increase in atomic heat with rise in temperature lies in the supposition of new degrees of freedom coming into existence. We cannot, however, imagine a "fractional" degree of freedom. It must either exist definitely, or not at all. One would expect, therefore, that the atomic heat should rise by *steps* as the temperature rises. All observations, however, have shown that the increase in atomic heat is a perfectly *continuous* function of the temperature. Leaving the problem of specific or atomic heats, let us turn to another important problem, namely, that of thermal radiation; for it was through investigation carried out in this field that the modifications of the principle of equipartition were eventually introduced, which in the hands of Planck and Einstein have permitted a satisfactory explanation to be given of the discrepancies hitherto existing between theory and experiment, not only in the domain of radiation itself, but likewise in that of the heat content of solids. Whether these modified views form the ultimate solution of the problem, it is at present impossible to say. They represent, at any rate, a fundamental stage in the development of the subject.

Application of [Classical] Statistical Mechanics to Radiation.

We are here concerned with temperature radiation only. A definition of this term has already been given together with a short account of the radiation laws in Chap. XIV. of Vol. II.

In studying the question of radiation, that is of the exchange of radiant energy between matter and ether, it is necessary, of course, to limit our consideration to the equilibrium state. If an enclosed material system is maintained at a temperature T, the interior of the system contains energy constantly radiated to and from the boundary. When these energy exchanges arrive at equilibrium each cubic centimetre of the system contains energy in what we may call the undulatory form. The problem is how to calculate the *most probable* distribution of the energy between the various wave-lengths not only for the single temperature T but for any temperature; for the equilibrium state may be defined as that for which the distribution of energy (at the given temperature) between the various wave-lengths is the most probable. To work out this statistical problem we must know something about the number of degrees of freedom possessed by the matter and by the ether (present throughout the matter) respectively. It will now be shown that absolutely different results are arrived at, according as to whether we regard the ether as continuous (*i.e.* structureless) or regard it as having a structure. Let us first consider the ether as continuous. In this case the ether is a medium capable of vibrating in an *infinite* number of ways the wave-lengths propagated throughout it having all possible values between o and ∞ . This is the same thing as saying that the

ether possesses an *infinite* number of degrees of freedom. Matter imbedded in the ether has on the other hand a *finite* number of degrees of freedom in virtue of its discontinuity, *i.e.* in virtue of its discrete or heterogeneous structure. If now we apply the principle of equipartition of energy to such a system composed of both matter and ether, it is clear that the ether will take all the energy (since its number of freedoms is infinite) leaving none at all for the matter.

The following mechanical analogy is suggested by Jeans. Let us suppose that we have a number of corks held together by elastic and floated upon the surface of still water. Cause the corks to move violently to and fro. Waves will be formed, *i.e.* energy will be given out from the cork system to the water by this kind of "radiation," as well as by friction, until finally the corks come to rest. All the energy originally given to the corks has now passed to the water. Permanent movement of the corks is unthinkable. It will be observed that the cause of this lies in the fact that the corks are large units compared with water molecules; in fact, the water is a sensibly continuous medium compared with the coarse-grained structure consisting of corks. It is impossible therefore to conceive of an equilibrium being set up as regards energy interchange between matter and ether except at the absolute zero of temperature. In other words, we cannot deduce any radiation law. It is clear, therefore, we must follow out some other line of reasoning. Let us take the second case, namely, the assumption that the ether does possess a structure. On this basis the number of degrees of freedom of the ether is no longer infinite, and it is possible to conceive of equilibrium states being reached at different temperatures as a result of energy transfer between matter and ether. If we think of the ether as possessing a fine-grained structure, it follows that the waves which can be propagated by such a medium must not become shorter than a certain limiting size λ_0. It is easy to see this by analogy. Waves which can be transmitted by a material system (sound waves, for example) must be great compared with the distance of the molecules which compose the system, as otherwise the waves would not be transmitted at all. Similarly, we must suppose that even the shortest light waves which we know of must be large compared with the grain structure of the ether itself. If this structure exists it ceases to be legitimate to speak of infinitely short waves in the mathematical sense. The shortest conceivable waves must be of the order of magnitude of the distance apart of the "molecules of the ether".

Starting out with the idea that the number of degrees of freedom possessed by the ether is finite, Jeans has shown that by applying the principle of equipartition of energy, the energy distributes itself in the normal spectrum in such a way that the intensity—corresponding to a region lying between λ and $\lambda + d\lambda$—is proportional to the temperature and inversely proportional to the fourth power of the wave-length. That is, the energy in the spectrum will so distribute itself that it will be almost entirely confined to the region of extremely short wave-lengths. As a matter of fact, however, this is not the real distribution of energy

in the spectrum. It has been shown experimentally that the intensity of energy radiating from a black body and in equilibrium with the body shows a maximum for waves in the infra-red region at ordinary temperatures, and vanishes almost completely for very long or very short waves. Representing it graphically we obtain a curve containing a maximum, as already shown in Fig. 53, Vol. II. On the other hand, the theoretical expression for the distribution of radiation energy, referred to above (which expression is identical with Rayleigh's radiation law, already stated in Chap. XIV., Vol. II., *viz.* $4\pi k T \lambda^{-4} . d\lambda$), yields a curve which contains no maximum but rises rapidly as the wave-length diminishes.

We are considering the case in which wave-lengths of all magnitudes exist between the infinitely long denoted by the symbol λ_∞ and the limiting value λ_0, but none shorter than this. If we integrate the Rayleigh-Jeans expression between the limits λ_0 and λ_∞, we obviously obtain an expression for the total radiant energy in the enclosure. The integration leads to the expression—

$$\frac{4}{3}\frac{kT}{\lambda^3_0}.$$

It follows from this expression that only one-eighth of the total energy will be of wave-length greater than $2\lambda_0$, whilst seven-eighths reside in wave-lengths between $2\lambda_0$ and λ_0 itself. In the case of the ether—if we give it a structure at all—the size of its grains must be considerably less than 10^{-7} cm. (the order of magnitude of a gas molecule). Taking this value, however, as applying to the ether grains, it follows that no wave-length shorter than 10^{-7} cm. can be transmitted. (As a matter of fact we know that X-rays are only about one-tenth of this.) Even with this limit to the wave-length it can be shown on the basis of the Rayleigh-Jeans formula that only one-millionth of the total energy would reside in wave-lengths of the order 10^{-5} cm. and longer. This is quite contrary to what is observed, for the greater part of the energy is known to lie in the region 10^{-4} cm. We conclude, therefore, that the assumption that the number of degrees of freedom of the ether is not infinite, is in itself insufficient to yield an expression (involving the equipartition principle) which will agree with experiment. We are forced to the conclusion, therefore, that the principle of equipartition itself is not applicable to the problem of distribution of radiant energy between matter and the ether. The result obtained on the equipartition basis always gives a partition of energy of such a kind that the energy is almost entirely confined to the short wave-lengths, and in the limit, *i.e.* if the ether be structureless, the energy goes completely into the ether and no distribution is possible at all. Experiment shows, on the other hand, that distribution certainly does exist, and furthermore, the distribution does not require that all the energy shall be located in the shortest wave-lengths; on the contrary, the distribution is such that very little energy is distributed among the very short or the very long waves, the greater part of it belonging to waves of intermediate magnitude. This

is indicated by the maximum in the intensity curve obtained in measurements of the amount of energy radiated from a heated body.

In the foregoing we have considered a number of problems, atomic heats of solids, molecular heats of gases, and radiation phenomena, from the point of view of classical statistical mechanics as expressed in the principle of equipartition of energy between degrees of freedom. In each case we find that the conclusions arrived at on this basis hold over a limited region, but fail to give a complete explanation of the phenomena observed. It is obvious that some additional hypothesis must be introduced, or rather, we must be prepared to discard the principle of *equi*partition and substitute for it some other kind of partition law. An attempt to do this has been made by Planck in his quantum hypothesis, which will be discussed in the following chapter.

CHAPTER II.

Introductory—Planck's concept of quanta—Planck's radiation formula.

The fundamental modification introduced by Planck consists in discarding the principle of *equi*partition of kinetic energy. The equipartition principle assumes interchange of energy in a continuous manner, *i.e.* without any lower limit to the amount of energy transferable. Planck assumes, on the other hand, that the exchanges of energy between matter and ether, instead of taking place in any proportion whatsoever, can only take place by steps, that is, in multiples of some small energy unit, the energy unit itself being a function of the vibration frequency concerned. We might regard radiant energy itself as possessing a structure. Planck himself regards the matter from a different standpoint. It would be more correct to say that the definite concept of radiant energy itself being discrete in nature is that upheld by Einstein, a view which has been given a clearer physical basis by J. J. Thomson, who considers a radiant-energy unit or "quantum" as a region of periodic disturbance travelling along a Faraday tube. In place of a continuous ether, we have therefore to substitute a number of stretched strings of ether, each string being a Faraday tube differentiated in some (practically unknown) way from the "space" surrounding it. This statement, is, however, to be taken rather as a rough material analogy than as an exact description or formulation, for any exact description is at the present time impossible. Planck, on the other hand, lays stress not on the question of the ultimate structure of radiant energy itself so much as on the *mode* of its absorption and emission by matter. The energy radiated by one element of a black body is partially absorbed by other elements. Each one of the vibrators, or "resonators," as Planck calls them, which constitute the material element in question, can only emit (and absorb) energy in certain fractions. (This at any rate is Planck's first position; we shall see later that he has modified the above view.) A word here about the Planck resonators. It was pointed out in the chapter on photochemistry in Vol. II. that the vibrating particles which produced visible and ultra-violet light were much smaller than the atoms of the substance and were therefore in all probability the electrons. The amount of energy contributed to the "total" spectrum by the visible or ultra-violet region has been shown by experiment (*cf.* Lummer and

Pringsheim's curve, Fig. 53, Vol. II.) to be a very small fraction of the whole (even at fairly high temperatures). The main part of the energy is confined to the infra-red region. These long waves are considered as emitted and absorbed by the *atoms* of the substance being set in vibration. These statements apply only to the continuous spectrum given out by a black body in the first instance and in general by heated metals. Planck's resonators for the infra-red may therefore be identified with the atoms (electrically charged); for the ultra-violet, with the electrons. But Planck in the theoretical treatment of the subject has regarded his resonators as *linear*, that is, he only considers the energy caused by vibration in a single direction. Such a vibration entails one degree of freedom. If we were to apply the equipartition principle to a system of such linear resonators, to each resonator, we would ascribe RT units of energy made up of $\frac{1}{2}$RT kinetic energy and an equivalent quantity of potential. It is only for extremely long waves that the equipartition principle holds (as is shown by the degree of applicability of Lord Rayleigh's formula for radiation), and that only for a limited temperature range. *The essence of Planck's view is that it discards the equipartition principle.* It will be noted that the linear resonators of Planck are considered to possess only one-third of the total vibrational energy of the actual atoms (of a solid), each of which possesses three degrees of freedom—as already pointed out in connection with the values for atomic heat.

According to Planck, the material resonators considered do not react with, or are not influenced by, *infinitely* small quantities of radiation energy, using the word infinitely in its strict sense. Planck's hypothesis may be stated thus: *It is necessary that the energy attains a finite value* ϵ *in order that the resonators composing the material system may be able to absorb it or emit it.* (As already mentioned, Planck later modified this statement by supposing absorption to be continuous, but emission discontinuous, *i.e.* in quanta.) It will be clear how this hypothesis modifies the principle of equipartition of energy among various degrees of freedom. To any degree of freedom which actually possesses energy we cannot ascribe less than one quantum (ϵ), and the actual quantity possessed will be an integral multiple of one quantum. With this distribution of energy some of the degrees of freedom may possess no energy at all, *i.e.* the *equi*partition idea breaks down.

The term "the quantum" requires now to be considered. Although we speak of this as the unit of (radiant) energy, it must be clearly understood that *it is* NOT *a fixed and constant quantity of energy.* According to Planck, the quantum ϵ, *i.e.* its size or magnitude, is a function of the vibration frequency (either of the radiation, supposing this to be monochromatic, or what amounts to the same thing, the frequency of the resonator). In fact, according to Planck, there is direct proportionality between the magnitude of ϵ and the frequency ν, this proportionality being expressed in Planck's fundamental relation—

$$\epsilon = h\nu$$

where h is a universal constant (Planck's constant) having the numerical value $6{\cdot}5 \times 10^{-27}$ erg-seconds.[1]

Now the *smaller* the unit the *greater* the probability that a resonator will possess at least one or some quanta. If we consider a material system, made up of molecules, atoms, and electrons, such a system possesses resonators of various dimensions, *i.e.* capable of vibrating with different frequencies. Such a system can absorb or emit a range (or spectrum) of vibration frequencies. Considering the very short waves, *i.e.* large vibration frequency, the quantum ϵ corresponding to this is large, and hence the chance that a resonator possesses even one quantum of this size is less than in the case of longer waves, where each quantum is a smaller magnitude. Less energy of the short wave type will therefore be emitted than that of the longer wave type. That is, the energy of the radiation emission curve falls off in the short wave region. In this way Planck explains the observed diminution in energy emitted in the visible and ultra-violet region, as shown in Lummer and Pringsheim's curves. Further, in the region of extremely long waves ν is relatively very small, and hence the size of the unit ϵ is small, so that for extremely long waves the actual energy contribution made by this region will be small. We should therefore expect on Planck's view the energy wave-length curve to pass through a maximum, as is actually the case.

Starting out with Planck's hypothesis of the discrete nature of absorption and emission of radiation, it is now necessary to see what radiation formula may be deduced; in other words, what theoretical expression can be deduced for the distribution of energy in the spectrum of a body emitting temperature-, *i.e.* black-body-radiation. For an exact and complete account, the reader is referred to Planck's *Theory of Heat Radiation*. We can only here attempt an abbreviated and approximate deduction, based upon a new method employed by Jeans (*Phil. Mag.*, **20**, 953, 1910).

If a vibration—that is, a very small spectral region lying between λ and $\lambda + d\lambda$, which corresponds experimentally to monochromatic radiation—can possess the following amounts of energy, *viz.* 0, ϵ, 2ϵ . . . etc., then the ratio of the probabilities of these events, as in the usual gas theory calculations, is—

$$1 : e^{-\epsilon/k\mathrm{T}} : e^{-2\epsilon/k\mathrm{T}} : \text{etc.}$$

where e is the base of natural logarithms, k a constant, namely, the gas constant per molecule, and T the absolute temperature. This means that if we represent by "1" the number of vibrations possessing no energy at all, then the number of vibrations, each of which possesses one unit of magnitude ϵ, will be $e^{-\epsilon/k\mathrm{T}}$, and so on. Instead of thinking of vibrations in "space," let us think of the resonators or vibrations of

[1] Planck (*Annalen der Physik*, [4], **4**, 553, 1901) has shown that the magnitude of ϵ is a function of ν by applying Wien's displacement law to an expression obtained by him for the entropy of a system. The reader should also consult Planck's *Theory of Heat Radiation*, 2nd edition.

matter which can emit or absorb such vibrations. Let us suppose that the material system consists of a great number of similar vibrators (emitting and absorbing the wave-length λ), each acting independently, then if we represent by unity the number of such resonators which possess no energy, the term $e^{-\epsilon/kT}$ gives the number of resonators possessing ϵ units each, etc. If out of N such resonators under consideration M have zero energy, the number of resonators, each of which has energy ϵ, is $Me^{-\epsilon/kT}$, the number having energy 2ϵ is $Me^{-2\epsilon/kT}$, and so on. Hence, for the total—

$$\begin{aligned} N &= M + Me^{-\epsilon/kT} + Me^{-2\epsilon/kT} + Me^{-3\epsilon/kT} + \text{etc.} \\ &= M(1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \text{etc.}) \\ &= \frac{M}{(1 - e^{-\epsilon/kT})}. \end{aligned}$$

And if $\Sigma\overline{U}$ is the total energy of the N resonators—

$$\begin{aligned} \Sigma\overline{U} &= M \times 0 + \epsilon \times Me^{-\epsilon/kT} + 2\epsilon \times Me^{-2\epsilon/kT} +, \text{ etc.} \\ &= \frac{Me\epsilon^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})^2}. \end{aligned}$$

Substituting the value for N already given, we obtain—

$$\Sigma\overline{U} = \frac{N\epsilon}{e^{+\epsilon/kT} - 1}.$$

If we now substitute $h\nu$ for ϵ, we obtain—

$$\Sigma\overline{U} = \frac{Nh\nu}{e^{h\nu/kT} - 1}.$$

And for the energy of one such resonator we obtain the *mean* value—

$$\overline{U} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

The same expression may be obtained in a different manner (*cf.* Appendix II.).

So much for the energy of a single vibrating resonator in radiation equilibrium with its surroundings, the expression being based on the hypothesis that energy is made up of units, the magnitude of a unit being directly proportional to the vibration frequency of the resonator. We have now to see the connection between this term $\overline{U}$ and the radiation density u_ν, that is, the quantity of monochromatic radiation (frequency ν) energy per c.c. of radiated space. Although u_ν is usually referred to as the radiation density, *i.e.* energy per unit volume, the term u_ν itself has not got the dimensions of energy/volume. The correct expression for radiation density is $u_\nu d\nu$, where $d\nu$ represents a narrow strip of the spectrum virtually monochromatic. In using the symbol u_ν for radiation density the quantity $d\nu$ is implied. Physically a single wave-length has no meaning; we always work with a very narrow strip of spectrum containing the wave-length or frequency denoted by λ or ν.

[In actual practice a heated body does not give out monochromatic radiation, but a complete spectrum. We shall define u_ν in different terms later, though still equivalent to the above.]

Planck has shown on the basis of the classical electro-magnetic theory (which therefore introduces no unitary hypothesis) that u_ν and $\bar{U}$ are connected by the relation—

$$\bar{U} = \frac{c^3}{8\pi\nu^2} \cdot u_\nu \cdot \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[*Cf.* Planck, *Annalen der Physik*, [4], **4**, 560, 1901; Lindemann, *Brit. Ass. Rep.*, 1912. If we take $\lambda = 800\mu\mu$ as a mean value for a wave-length in the red part of the spectrum, it is easily calculated from this formula that $\bar{U} = 8u$ (approx.). Similarly for the violet end of the spectrum, taking $\lambda = 400\mu\mu$, one finds $\bar{U} = 2u$ (approx).]

By combining the two expressions obtained above, the mean value of the density of energy radiated from a single resonator in a system consisting of a large number of similar resonators, all emitting monochromatic light of frequency ν (*i.e.* between the limits ν and $\nu + d\nu$), is given by the expression—

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \cdot d\nu.$$

This is one of the forms of Planck's Radiation Formula.

We wish now to change the shape of this expression a little, in order to be clear about the relation of the term u_ν and the term E_λ, which latter we have already met with in Wien's radiation formula (*cf.* Chap. XIV., Vol. II.).

The total energy (say in ergs) radiated per second from unit area of a black body emitting a continuous spectrum covering the wave-lengths 0 to ∞ has been denoted by S. This is the term which appears in Stefan's Law, *viz.* $S = \sigma T^4$, the temperature of the source being T and the radiation purely "temperature" radiation. Now S is the quantity of energy which would be present in an imaginary cylinder, 1 square centimetre base and length 3×10^{10} cms. (since 3×10^{10} cms. is the distance which the radiation will travel in one second). The cylinder is supposed to be placed with its base on the radiating body and extending out into space. The volume of this cylinder is 3×10^{10} c.c., and since this contains S ergs of energy the space density of the radiation, *i.e.* the amount of energy per c.c. is $\frac{S}{3 \times 10^{10}}$ erg. Denoting the space density of the energy by E, we have $E = \frac{S}{3 \times 10^{10}}$ or $S = 3 \times 10^{10} E$, the term E referring, of course, to the entire range of wave-lengths between 0 and ∞ emitted by the body. This total density E may be expressed thus—

$$E = \int_{\lambda=0}^{\lambda=\infty} \frac{\partial E}{\partial \lambda} . d\lambda.$$

Let us write $E_\lambda = \frac{dE}{d\lambda}$, then $E = \int_0^\infty E_\lambda d\lambda$.

It will thus be seen that E_λ is a *rate* (the rate of change of E with λ). We might also define it as the *density* of the energy radiated from a spectral region the wave-length limits of which differ by unity. This, though correct, is physically inconceivable. It would entail the existence of a spectrum the wave-length limits of which differ by 1 cm., a difference enormous compared to any actual limits reached. It is therefore much less confusing to think of E_λ as being the small energy-density increment ΔE divided by the correspondingly small spectral width $\Delta\lambda$ (or more accurately $\frac{\partial E}{\partial \lambda}$ as above). The expression $E_\lambda d\lambda$ or $\frac{\partial E}{\partial \lambda} d\lambda$ is therefore the energy-density of the radiation between λ and $\lambda + d\lambda$. Planck gives an analogous significance to the term $u_\nu d\nu$. Thus the energy-density of the total spectrum may be written—

$$E = \int_{\nu=0}^{\nu=\infty} \frac{\partial E}{\partial \nu} d\nu$$

or writing $u_\nu = \frac{\partial E}{\partial \nu}$, $E = \int_0^\infty u_\nu d\nu$.

The term u_ν is also a rate, or it may be defined as the density of the energy radiated from a spectral region, the limits of the vibration frequency differing by unity. Numerically u_ν is of quite a different order of magnitude from E_λ. Thus, since $\lambda = \frac{c}{\nu}$, where c is the velocity of light, it is evident that $\frac{d\lambda}{d\nu} = -\frac{c}{\nu^2}$, so that on increasing ν by unity (*i.e.* corresponding to the production of $u_\nu \times 1$ energy-density units) the wave-length decreases by the amount $\frac{c}{\nu^2}$. This gives a result of the order 10^{-18} in the case in which the infra-red wave-length region $\lambda = 1\mu$ is considered. Since E_λ is the energy-density corresponding to a wave-length difference of *unity*, the term E_λ is $10^{18}\, u_\nu$ for the region in which the vibration frequency differs by unity.

The shortest wave-length physically possible, *i.e.* the shortest wave-length capable of being emitted or absorbed by an atomic-electronic mechanism (such as that associated with a molecule), is of the order of magnitude of very hard X-rays, namely, 10^{-9} cm. This sets a limit, therefore, to the width of spectrum which can be regarded as possessing a physical meaning. It is interesting to see what this limiting width is

when expressed in terms of the difference of the frequencies between the "edges" of the strip. Let us suppose that the strip is chosen in the middle of the visible spectrum. The mean value of λ is then $0{\cdot}6\mu$ or 6×10^{-5} cm., the limiting value to be ascribed to $d\lambda$ being 10^{-9} cm. The frequency difference $d\nu$ which corresponds to $d\lambda$ is given by—

$$d\nu = -\frac{c}{\lambda^2} \cdot d\lambda.$$

That is, for the case considered,

$$-d\nu = \frac{3 \times 10^{10} \times 10^{-9}}{36 \times 10^{-10}} = 10^{10}.$$

Hence, in the region of the spectrum referred to, the smallest width to which we can attach a physical meaning corresponds to a frequency difference of the order 10^{10}. The actual or absolute frequency in the middle of this strip is of the order 5×10^{14}.

In bolometric or spectro-photometric determinations we measure the energy ΔS radiated per second by a small region or strip of a continuous spectrum which lies between λ and $\lambda + \Delta\lambda$. Since $S = 3 \times 10^{10} E$, and therefore $\Delta S = 3 \times 10^{10} \Delta E$, we can calculate $\frac{\Delta E}{\Delta \lambda}$ which in turn is identical with E_λ. We now wish to express the radiation formula of Planck in such a way as to allow of convenient comparison between E^λ observed and its value as given by the formula. To do this let us rewrite the formula already given :—

$$u_\nu d\nu = \left(\frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1}\right) d\nu.$$

Remembering that $u_\nu d\nu = E_\lambda d\lambda$, and further that $d\lambda = -\frac{c}{\nu^2} d\nu$, we obtain directly—

$$E_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT} - 1} \quad . \quad . \quad . \quad . \quad (2)$$

which is the more usual form of Planck's equation for the distribution of energy throughout the spectrum. As already pointed out, we can compare the observed and calculated values of E_λ for a whole series of small regions and thus test the equation over the complete spectrum. It has been found that the above formula reproduces the actual energy distribution from a black body in an extremely accurate manner, being in fact the most satisfactory equation yet proposed. The principal experimental investigations are those of Lummer and Pringsheim (*Verh. d. Deutsch. physik. Gesell.*, **1**, 23 and 215, 1899; **2**, 163, 1900), Rubens and Kurlbaum (*Sitzungsber. d. K. Akad. d. Wissenschaft zu Berlin*, **41**, 929, 1900; *Annalen d. Physik*, [4], **4**, 649, 1901), Paschen (*Annalen d. Physik*, [4], **4**, 277, 1901), and the more recent measurements of W. Coblentz (*Bull. Bur. Standards*, 1914, **10**, p. 1).

By way of illustration a few of Paschen's results may be quoted. The extent of the spectrum examined was from 1 to 8·8μ (*i.e.* the infra-red region), measurements being carried out by means of the bolometer. Using a fluorite prism (which is more transparent than quartz) successive parts of the spectrum could be isolated. The radiating body consisted of a hollow vessel or cylinder, electrically heated to any desired temperature, the cylinder being either of platinum or porcelain with or without a coating of copper oxide. In the following table i denotes the magnitude of the swing of the galvanometer needle, a certain swing corresponding to a certain amount of energy communicated by the radiation to the bolometer. After calibrating the apparatus, Planck's formula can be used to calculate values of i for different wave regions, and these may be compared with experiment.

TABLE I.—λ = 1·0959 μ. Width of spectrum isolated = 3′. Temperature of surroundings = 9·8° C.

T = Temperature of Radiator =		1333·4.	1553·1.	1328·3.	1038·7.
i	Observed	60·6	252·6	59·3	3·65
	Calculated from Wien's equation	61·44	252·5	59·14	3·61
	Calculated from Planck's equation	61·27	249·4	58·97	3·68

TABLE II.—λ = 8·7958 μ. Width of spectrum isolated = 6′. Temperature of surroundings = 15·1° C.

Temperature of Radiator =		1458·6.	1069·8	844·4.	625·6	483·1.
i	Observed	131·7	74·43	44·51	20·46	9·22
	Wien's equation	90·40	59·79	39·52	19·86	9·08
	Planck's equation	129·1	73·75	44·83	20·90	9·22

It will be observed that Planck's formula is much more applicable than Wien's for high temperatures and long waves. Besides the infra-red region, the experiments of Paschen and Wanner, as well as those of Lummer and Pringsheim, on radiation from the visible spectral region, have shown that Planck's formula holds here also within the limits of experimental error. In addition to the direct method of testing Planck's formula outlined above, its validity is further shown by the fact that we can deduce from it directly Wien's *displacement law* (*viz.* $\lambda_{max.} \times T$ = constant, and $E_{max.}$ = constant $\times T^5$), and Stefan's total radiation law—

$$\left(S = \text{const.} \times T^4, \text{ where } S = 3 \times 10^{10} E = 3 \times 10^{10} \int_0^\infty E_\lambda d\lambda\right),$$

both of which have been experimentally verified. Planck's expression is thus a very comprehensive one.[1]

Some Numerical Values.

At this point it is of interest to calculate the values of the two fundamental constants h and k which occur in Planck's equation. h is the universal proportionality-factor connecting the energy ϵ of a quantum with the frequency ν; k, as will be shown later, is the gas constant R, reckoned not for a gram-mole but for a single molecule. The calculation may be carried out as follows.

Kurlbaum (*Wied. Ann.*, **65**, 759, 1898) has found by experiment that the total energy emitted from 1 square centimetre of a "black body" in 1 second, the temperature of the body being 100° C. and that of the air being taken as 0° C., amounts to 0·0731 watt/cm.^{2}, that is—

$$S = S_{100^\circ\,C.} - S_{0^\circ\,C.} = 4{\cdot}2 \times 7{\cdot}31 \times 10^5 \text{ ergs/cm.}^2\text{-sec.}$$

By applying Stefan's Law we obtain—

$$S = \sigma(373^4 - 273^4).$$

Hence $$\sigma = \frac{4{\cdot}2 \times 7{\cdot}31 \times 10^5}{(373^4 - 273^4)} \cdot \frac{\text{ergs}}{\text{cm.}^2\text{-sec.-degrees}^4}.$$

The physical significance of σ is evidently the total radiation emitted from a black body per second, when the temperature difference between the black body and the surroundings is 1 degree, the temperature of the black body being 1° absolute, the surroundings being at 0° absolute. Corresponding to this emission at 1° absolute,

[1] To emphasise further the fact that Planck's formula is at variance with the principle of *equi*partition of energy among various degrees of freedom, it is interesting to calculate the energy of an electron vibrating with a frequency identical with that of the ultra-violet region when light is emitted, and compare this energy with the energy of an atom or of a gaseous molecule possessing the mean kinetic energy characteristic of ordinary temperature (say 300° absolute), (*cf.* J. Stark, *Zeitsch. physik. Chem.*, **86**, 53, 1913). The frequency ν for the ultra-violet region will be about 5×10^{14} per second. Planck's expression for the mean energy of a single resonator is, as we have already seen—

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

For ordinary (low) temperatures—T = 300°—this expression reduces to $\bar{U} = h\nu e^{-\frac{h\nu}{kT}}$, since ν is large and T small. The mean energy of an electron resonator is therefore $\bar{U}$, where $\bar{U} = 1 \times 10^{-16}$ ergs. The mean kinetic energy of a gas molecule at the ordinary temperature $= \frac{3}{2}kT = 6 \times 10^{-14}$ ergs, so that instead of equipartition of energy we find that the energy of the electron vibrating in the atom or molecule is only one five-hundredth part of the mean kinetic energy of translation of the molecule itself.

we see that E, *i.e.* the total energy density, is $\frac{\sigma}{3 \times 10^{10}}$, that is—

$$E_{1^\circ \text{ abs.}} = \frac{4{\cdot}2 \times 7{\cdot}31 \times 10^5}{3 \times 10^{10}(373^4 - 273^4)} = 7{\cdot}061 \times 10^{-15} \frac{\text{ergs}}{\text{c.c.}}.$$

Now $E = \int_0^\infty E_\lambda d\lambda$, or $\int_0^\infty u_\nu d\nu$ and E_λ or u_ν is given by Planck's expression. Using Planck's expression in the form in which u_ν occurs, we get—

$$E_{1^\circ \text{ abs.}} = \int_{\nu=0}^{\nu=\infty} u_\nu d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k} - 1}$$

the term T being omitted in the final expression, since it is simply unity. The integration may be effected by series, and we obtain finally—

$$E_{1^\circ \text{ abs.}} = \frac{48\pi k^4}{c^3 h^3} \times 1{\cdot}0823.$$

Setting this equal to the "observed" value of $E_{1^\circ \text{ abs.}}$, *viz.* $7{\cdot}061 \times 10^{-15}$, we obtain—

$$\frac{k^4}{h^3} = 1{\cdot}1682 \times 10^{15} \quad . \quad . \quad . \quad . \quad (3)$$

Further, Lummer and Pringsheim (*Verh. d. Deutsch. physik. Gesell.*, **2**, 176, 1900) have determined the value of $\lambda_{max.}$ T, where $\lambda_{max.}$ is the wave-length corresponding to the maximum value of E_λ from a black body radiating at a given temperature. The expression $\lambda_{max.} \times T$ is a constant independent of temperature as Wien has shown, the numerical value found by Lummer and Pringsheim being 0·294 cm. degrees. Now, by differentiating Planck's formula (equation (2)) with respect to λ, and putting the differential equal to zero, when $\lambda = \lambda_{max.}$ we obtain—

$$\left(1 - \frac{ch}{5k\lambda^{max.}\,T}\right) e^{ch/k\tau\lambda_{max.}} = 1$$

whence $\lambda_{max.} \times T = \frac{ch}{4{\cdot}9651k}$

or $$\frac{h}{k} = \frac{4{\cdot}9651 \times 0{\cdot}294}{3 \times 10^{10}} = 4{\cdot}866 \times 10^{-11} \quad . \quad . \quad (4)$$

By combining equations (3) and (4) we obtain finally—

$$h = 6{\cdot}55 \times 10^{-27} \text{ erg/sec.}$$
$$k = 1{\cdot}346 \times 10^{-16} \text{ erg/degree.}$$

Millikan (*Proc. Nat. Acad. Sci.*, **3**, 314 (1917)) gives as the most accurate value of the charge *e* on an electron, the quantity $4{\cdot}774 \pm 0{\cdot}005 \times 10^{-10}$ electrostatic units. Knowing this quantity and the value of *e/m*, *viz.* $1{\cdot}767 \times 10^7$, and also knowing Rydberg's con-

stant for the Balmer series in the hydrogen spectrum,[1] *viz.* $3{\cdot}290 \times 10^{15}$ according to Millikan, the value of Planck's constant h may be calculated with a high degree of precision. The value given by Millikan is—

$$h = 6{\cdot}547 \pm 0{\cdot}011 \times 10^{-27}$$

which is in close agreement with that "observed" by Millikan (6·56) and by Webster (6·53).

The Significance of the Constant k, and a Determination of the Number of Molecules in one gram-molecule.

Consider once more the Planck expression for the energy of vibration of a large number of similar resonating particles emitting monochromatic radiation, *viz.*—

$$\Sigma\overline{U} = \frac{N\epsilon}{e^{\epsilon/kT} - 1}.$$

The expression $e^{\epsilon/kT} - 1$ may be expanded thus—

$$\frac{\epsilon}{kT} + \frac{1}{2}\left(\frac{\epsilon}{kT}\right)^2 + \text{higher powers.}$$

If now we are dealing with a system vibrating at very high temperature it will be seen that the above expression becomes $\frac{\epsilon}{kT}$. That is, at high temperatures—

$$\Sigma\overline{U} = \frac{N\epsilon}{\frac{\epsilon}{kT}} = NkT.$$

Exactly the same result is obtained at less high temperatures if the system is vibrating very slowly, for in this case ν is small (relatively), and since $\epsilon = h\nu$ the quantity ϵ is likewise small. In both cases the quantity ϵ vanishes from the expression for the sum of the energies of the vibrating particles, this energy being simply proportional to the absolute temperature. Under these conditions we reobtain the results of the ordinary kinetic theory, *i.e.* the principle of equipartition of energy, it being no longer necessary to consider the energy as other than continuous. The principle of equipartition of energy is therefore true as a limiting case for large values of T, and for small values of ν. Suppose that we are dealing with a solid radiating energy at a temperature sufficiently high that the energy of vibration of the resonators could be represented by NkT. The resonators, as employed by Planck, are linear, *i.e.* they possess 1 degree of freedom, to which one would ascribe (if the equipartition principle applied, *i.e.* if T is sufficiently high) $\frac{1}{2}$RT kinetic and $\frac{1}{2}$RT potential, in all RT units of energy per gram-mole or

[1] *Cf.* Bohr's theory of the atom (Chap. V.), according to which Rydberg's constant $= 2\pi^2 e^4 m/h^3$.

gram-atom, if a monatomic solid be considered, and if the atoms be identified with the resonators.[1]

Hence, the term $\Sigma\bar{U}$ reckoned for N "linear" atoms where N is now regarded as the number of atoms in a gram-atom (or molecules in a gram-mole) should be identical with RT. That is, $RT = kNT$, or $R = kN$. The constant k is therefore simply the gas constant reckoned for a single molecule.

We may see in another way that k has this significance. As has been pointed out already, Jeans[2] has shown that for very long waves the law of the partition of energy, or of energy-density between waves of different lengths, as expressed in a formula, must contain the wave-length term to the inverse fourth power. A similar formula was deduced by Lord Rayleigh on the classical theory, and holds well for the very long wave-length region. Jeans' equation is—

$$E_\lambda = 8\pi R_j T \lambda^{-4}$$

where R_j is here the gas constant reckoned for a single molecule. Now for this very long wave region we have seen that Planck's expression may be simplified, the term $\frac{1}{e^{h\nu/kT} - 1}$ becoming $\frac{kT}{h\nu}$ or $\frac{kT\lambda}{hc}$.

That is, Planck's equation becomes—

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{kT\lambda}{hc} = 8\pi kT\lambda^{-4}.$$

On comparing this with Jeans' equation, it is at once evident that the two become identical—and they must be identical if they are equally to reproduce experimental results in the long-wave region—if k is identical with R_j, *i.e.* k is the gas constant per single molecule. This may be tested at once by calculating N from the known value R (per mole), and from the value of k calculated from radiation data, using Planck's formula. It this way it is found that $N = 6{\cdot}175 \times 10^{23}$, a number which agrees very well indeed with the values obtained by Perrin and Millikan (*cf.* Vol. I., Chap. I.). This "radiation" method may therefore be regarded as a new and independent method of calculating the Avogadro constant. The value of N just given leads to a value for the charge on an electron, *viz.* $4{\cdot}69 \times 10^{-10}$ electrostatic units, which agrees well with Millikan's value, $4{\cdot}774 \times 10^{-10}$.[3]

[1] The actual atoms in solids vibrate with three degrees of freedom. For the present we are considering "linear" atoms or atoms possessing 1 degree of freedom.

[2] Jeans, *Phil. Mag.*, [6], **17**, 229, 1909.

[3] In the above calculation the value of k was obtained from radiation data. The most accurate because the most direct method of obtaining k is simply to divide R by N.

According to Millikan the most accurate value for N is $6{\cdot}062 \times 10^{23}$.

Hence $k = \frac{R}{N} = \frac{83{\cdot}2 \times 10^6}{6{\cdot}062 \times 10^{23}} = 1{\cdot}37 \times 10^{-16}$ ergs/degree.

Numerical Values of the Size of the Quantum ϵ in different Spectral Regions.

In the following table are collected some values of $(h\nu)$ extending over a wide range. The longest wave measured by Rubens, in 1910, was $\lambda = 90\mu$, though still longer waves have been measured more recently. The shortest wave-length measured is of the order $0{\cdot}1\mu$, or $100\mu\mu$ (Schumann).

Wave-length λ.	$\nu = \frac{c}{\lambda}$.	$\epsilon = h\nu$.
$\lambda = 90\mu$	$3{\cdot}3 \times 10^{12}$	$2{\cdot}1 \times 10^{-14}$ ergs
$\lambda = 6\mu$	5×10^{13}	$3{\cdot}3 \times 10^{-13}$,,
$\lambda = 2\mu$. (This is the region of maximum intensity when the body is at 1646° absolute)	$1{\cdot}5 \times 10^{14}$	$9{\cdot}9 \times 10^{-13}$,,
$\lambda = 0{\cdot}8\mu$. (This is approximately the limit of the visible red)	$3{\cdot}75 \times 10^{14}$	$2{\cdot}47 \times 10^{-12}$,,
$\lambda = 0{\cdot}4\mu$. (This is approximately the limit of the visible violet)	$7{\cdot}5 \times 10^{14}$	$4{\cdot}95 \times 10^{-12}$,,
$\lambda = 0{\cdot}2\mu$. (This is the limit obtainable with a quartz prism)	$1{\cdot}5 \times 10^{15}$	$9{\cdot}9 \times 10^{-12}$,,
$\lambda = 0{\cdot}1\mu$. Schumann rays	$3{\cdot}0 \times 10^{15}$	$1{\cdot}9 \times 10^{-11}$,,

The value of ϵ can thus vary from 10^{-11} to 10^{-14} ergs, according to the vibration frequency of the resonator, *i.e.* the vibration frequency of the radiation. As already pointed out, the resonators emitting short waves are probably electrons, those emitting long waves are probably the atoms. As regards the total energy emitted from a heated body, we can neglect the portion due to wave-lengths shorter than $0{\cdot}8\mu$, *i.e.* we can neglect the visible and ultra-violet regions. This is true, of course, only for bodies the temperature of which is not higher than 1600° C. If the temperature of the radiator be raised much higher than this, the contribution from the visible may no longer be negligible, since in accordance with Wien's displacement law the position of maximum energy emission shifts towards the shorter wave region the higher the temperature. A body with the temperature of the sun (say 6000° C.), radiating purely thermally (without chemical effects in addition, as is the case with the sun), would have its maximum emission of energy at $\lambda = 0{\cdot}5\mu$ approximately, *i.e.* in the blue-green region. It is of course quite impossible to realise a temperature so high as this under any experimental conditions.

In connection with Einstein's view of the quantum hypothesis, namely, the view that radiation itself consists of small units travelling through space, it is necessary to point out one important phenomenon which it is very difficult to reconcile with this view. The phenomenon is that of interference of light, when two beams starting in the same phase have traversed paths which differ in length. The difficulty of

expecting interference on the Einstein view is very considerable, especially when it is recalled that interference can be produced—as in certain experiments of Michelson—with a difference of path of 40 cms., a distance which is enormously great compared with one wave-length.

Planck's Later Quantum Hypothesis.

Planck's Modified Equation for the Energy of an Oscillator.

(*Cf.* Max Planck, *Ber. d. Deut. physik. Gesell.*, **13**, 138, 1911.)

The essential modification here introduced is that while emission of radiant energy takes place in quanta, and therefore discontinuously, absorption can take place continuously. Planck was led to consider this as more probable than the older view, one important reason having to do with the question of time. Supposing absorption took place in quanta only, then an oscillator might be exposed to radiation so weak as not to yield even one quantum, under which condition the oscillator would absorb no energy at all. This would be especially true for large values of ν (large units). Further, even in those cases in which absorption could occur, it is conceivable that in weak radiation there might be a time interval.

On the former view the energy U of an oscillator could be expressed by $U = n\epsilon$, where n is an integer. If absorption is continuous, the total energy can no longer be regarded as an exact multiple of ϵ, but could in general be regarded as consisting of $n\epsilon$ units plus a quantity ρ over. That is—

$$U = n\epsilon + \rho.$$

Now the limits for the value of ρ are zero and one ϵ. If we are considering a large number of oscillators ρ will have an average value $\frac{\epsilon}{2}$ or $\frac{h\nu}{2}$, so that we can write—

$$\overline{U} = n\epsilon + \frac{h\nu}{2}.$$

On the older view Planck's equation for U is—

$$\overline{U} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

which evidently corresponds to $n\epsilon$.

The new expression for $\overline{U}$ can therefore be written—

$$\overline{U} = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} = \frac{h\nu}{2}\left(\frac{2}{e^{h\nu/kT} - 1} + 1\right),$$

or

$$\overline{U} = \frac{h\nu}{2}\left(\frac{e^{h\nu/kT} + 1}{e^{h\nu/kT} - 1}\right).$$

Planck points out several consequences of this new expression.

When T = o, $\bar{U}$ is not = o, but = $\frac{h\nu}{2}$. This "residual energy" remains with the oscillator even at o° absolute. It cannot lose it since it cannot emit anything less than *one hν*. "At high temperatures and for long waves in the region where the Jeans-Rayleigh Law holds the new formula passes into the old."

For short waves (visible and ultra-violet region) $e^{h\nu/kT}$ becomes large compared with unity, and we have—

$$\bar{U} = \frac{h\nu}{2}.$$

As regards the question of the specific heats of solids considered in the following chapter, it is pointed out by Planck that measurements of specific heat cannot be used to compare the older and newer forms of $\bar{U}$ since C_v is $d\bar{U}/dT$, and differentiation removes the additional term $\frac{h\nu}{2}$. Planck doubts whether the new expression can be tested experimentally by any direct means.[1]

Up to this point the most important experimental evidence which we have considered in support of the quantum theory is the fact that Planck's radiation formula quantitatively reproduces experimental values over the entire range of the spectrum investigated. In the next chapter we shall deal with further experimental evidence in connection with the atomic heats of solids which likewise is strongly in favour of the concept of quanta.

[1] Planck refers to a paper by Stark (*Phys. Zeitsch.*, 9, 767 (1908)), on the application of the quantum theory to canal rays. As regards an attempt to distinguish between the old and new form of the quantum theory, see A. Einstein and O. Stern (*Annalen der Physik*, [4], 40, 551, 1913).

CHAPTER III.

(Physical equilibrium in solids)—Theory of atomic heats of solids—Equations of Einstein, Nernst-Lindemann, and Debye.

Einstein's Extension of Planck's Quantum Theory to the Calculation of Specific Heats of Solids (*Crystalline Substances*) *and Supercooled Liquids* ("*Amorphous Solids*"). (*Cf.* Einstein, *Annalen der Physik*, [4], **22**, 180, 1907.)

THE specific heat of a substance at constant volume is defined as the increase in total energy when the substance rises 1° in temperature. Let us take as our unit of mass the gram-mole or gram-atom (in the case of monatomic substances), and we then can write—

$$C_v = \frac{dU}{dT}.$$

NOTE.—U here stands for total energy possessed by the substance at a given temperature. It is not to be confused with the significance attached to U in the "elementary thermodynamical treatment" (Chap. I., Vol. II.), in which "U" stood for *decrease* in total energy due to chemical reaction.

Let us now restrict our attention to solids (or supercooled liquids), taking as particular instances the metallic elements. These, as we have seen, are regarded as monatomic, so that the gram-atom and gram-molecule are identical terms in these cases. Now we want to find out to what the total or internal energy of a metal is due. It is usual to regard the solid state as characterised by vibrations of the atoms about their respective centres of gravity. Such vibrations can, of course, take place in the three dimensions of space, *i.e.* each atom possesses three degrees of freedom. As we have seen, each vibration represents energy, one-half of which is kinetic, one-half potential, as long as the amplitude of the vibration is not too great. This vibrational energy is regarded as representing all the internal energy possessed by the atom, at least at low temperatures (at high temperatures the energy of vibration of the electrons inside each atom would have to be considered, but at ordinary temperature and at lower temperatures the total energy of the solid may be ascribed to the vibration of the atoms). We have already discussed this, and we have seen that on applying the principle of equipartition of energy the atomic heat of metals should be $3R = 5{\cdot}955$ cals. per degree, and that this should be independent of temperature. As already pointed out, this numerical value is certainly

approximated to at ordinary temperatures, but instead of being independent of temperature, it varies, becoming continuously smaller as the temperature is lowered. The question therefore which arises is how this variation with temperature is to be accounted for. Einstein in 1907 made the first successful attempt at the solution of this problem by suggesting that Planck's quantum theory—which Planck himself had applied with so much success to the problem of the emission of radiant energy—could also be applied to the vibrational energy of the atoms, *i.e.* to the total internal energy of the solid, the temperature coefficient of which is identical with the specific or atomic heat of the substance in question: Planck's expression for the average energy of vibration of a linear resonator (*i.e.* an atom vibrating along *one* of the dimensions of space) is, as we seen—

$$\overline{U} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

[It will be observed that we are employing Planck's earlier hypothesis.] The energy of vibration of an atom capable of vibrating along the three dimensions of space will be three times this quantity, and if we denote this average vibrational energy per gram-atom by U, we get—

$$U = \frac{3N h\nu}{e^{h\nu/kT} - 1}.$$

The significance of U is identical with that which has been ascribed to it in Chap. II., Vol. II., namely, the total energy per mole or gram-atom. In the case considered one-half of U is kinetic, one-half potential energy. N denotes the number of atoms in one gram-atom. On Planck's earlier view the vibrational energy possessed by each atom must be an even multiple of one quantum. On the "classical" view ("structureless energy," so to speak) we should say that all possible differences in energy content would manifest themselves in a system made up of a large number of vibrating particles. On applying the unitary theory of energy we must recognise that a number of atoms have no vibrational energy at all, *i.e.* are at rest. Of those vibrating the energy content cannot fall below the quantum ϵ', where ϵ' is three times Planck's quantum ϵ. We have, therefore, sets of atoms containing energy of the following amounts:—

$$0,\ \epsilon',\ 2\epsilon',\ 3\epsilon',\ \text{and so on.}$$

In order to bring the expression for U given above into the form used by Einstein, Nernst, and others, we shall make a slight change in the symbols. If we denote the ratio of Planck's two fundamental constants k and h by β_0,[1] we can write $\frac{h}{k} = \beta_0 = 4{\cdot}87 \times 10^{-11}$ C.G.S. units. Also, since $k = \frac{R}{N}$, where R = 1·985 calories, we can write $h\nu = \frac{R}{N}\beta_0\nu$.

[1] This is frequently written as β. The slight change is here introduced to prevent any confusion with β, one of the terms in Nernst's "heat theorem" equations of A and U.

The expression for U then becomes—

$$U = 3R \cdot \frac{\beta_0\nu}{e^{\beta_0\nu/T} - 1}.$$

It will be observed that this equation differs from the expression $3RT$ (obtained by applying the *equi*partition principle, energy being regarded as continuous), by the substitution of the term $\frac{\beta_0\nu}{e^{\beta_0\nu/T} - 1}$ in place of T.

Differentiating U with respect to T we obtain Einstein's equation for the atomic (or molecular) heat of a solid at constant volume, *viz.*—

$$C_v = \left(\frac{dU}{dT}\right)_v = 3R \cdot \frac{e^{\beta_0\nu/T} \cdot \left(\frac{\beta_0\nu}{T}\right)^2}{e(\beta_0\nu/T - 1)^2}.$$

On the "classical" view, the factor multiplied by $3R$ would have been

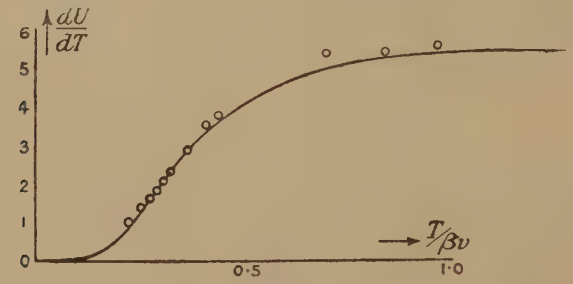

FIG. 5.

unity. The "correction" term will be seen to contain T and is therefore a function of temperature. On Einstein's theory one would expect the atomic heat itself to be a function of temperature, as is experimentally the case. Qualitatively, therefore, this marks a considerable advance over the older theory. It still remains to be seen whether the expression given really reproduces the values of C_v at various temperatures quantitatively. The shape of the curve for $\frac{dU}{dT}$ as given by Einstein's formula is shown in the accompanying figure (Fig. 5), in which the ordinates represent atomic heats and the abscissæ the temperature expressed in terms of $\frac{T}{\beta_0\nu}$. For any given substance the vibration frequency is taken to be a constant.

It will be seen from the figure that when $\frac{T}{\beta_0\nu} > 0{\cdot}9$ the term

$\frac{e^{\beta_0\nu/T} \cdot \left(\frac{\beta_0\nu}{T}\right)^2}{(e^{\beta_0\nu/T} - 1)^2}$ approximates to unity, so that the atomic heat becomes equal to 3R. Dulong and Petit's Law is, therefore, a consequence of Einstein's theory when the temperature is not too low. This region of temperature is evidently reached at room temperature in the case of the majority of metallic elements. As in radiation phenomena we see that the equipartition principle applied in the ordinary way yields results (in connection with atomic heat) which are in agreement with experiment when the temperature reaches a certain magnitude. Einstein tested his equation not on the data available in the case of a metal but on the diamond. Some of the results are given in the subjoined table. They are also indicated by circles in the figure. Einstein chose the experimentally determined value for C_v at $T = 331{\cdot}3°$ and hence calculated ν, using the value so obtained to calculate the values of C_v at other temperatures. The experimental data (quoted) refer, as a matter of fact, to C_p, *i.e.* the atomic heat at constant pressure. In the case of the diamond—though not so in other cases—the difference between C_p and C_v is small. In the following section we shall consider the question of the independent determination of ν and C_v respectively.

ATOMIC HEAT OF CARBON (DIAMOND).

T (absolute).	$T/\beta_0\nu$.	C_v calculated from Einstein's equation.	C_p observed (Weber).
222·4	0·1679	0·762	0·76
262·4	0·1980	1·146	1·14
283·7	0·2141	1·354	1·35
306·4	0·2312	1·582	1·58
331·3	0·2500	1·838	1·84
358·5	0·2705	2·118	2·12
413·0	0·3117	2·661	2·66
479·0	0·3615	3·280	3·28
520·0	0·3924	3·631	3·63
879·7	0·6638	5·290	5·29
1079·7	0·8147	5·387	5·39
1258·0	0·9493	5·507	5·51

Measurements of C_v of the diamond at low temperatures down to 30° abs. have been carried out by Nernst, who discovered the remarkable fact that the thermal capacity of this substance tends practically to zero, even at the temperature + 50° abs. Between this temperature and absolute zero, C_v or $\frac{dU}{dT} = 0$. We have already had occasion to point this out in connection with Nernst's heat theorem. From the shape of Einstein's curve (Fig. 5), it will be seen that C_v is tending towards zero at a temperature higher than 0° abs. It thus appears that,

as far as the diamond is concerned, Einstein's theory reproduces experimental values with very considerable fidelity. While giving full weight to such general agreement, it is necessary to point out that this agreement is far from being complete in many other cases. We shall return to this after having described in outline the experimental methods of determining C_v, and the characteristic vibration frequency ν.

Experimental Measurements of the Specific Heats of Solids, especially at Low Temperature.

(*Cf.* Nernst, *Journ. de Physique*, [4], **9**, 1910; Nernst, Koref, and Lindemann, *Sitzungsber. Berl. Akad.*, 1910, vol. 1, p. 247; *ibid.*, Nernst, p. 262; Nernst, *Annalen der Physik*, [4], **36**, 395, 1911.)

One form of calorimeter consisted of a heavy vessel of copper (about 400 grams in weight), the good thermal conductivity of such a mass of copper doing away with the necessity of stirring the substance, which is, of course, impossible in the case of solids. This was enclosed in a Dewar vacuum vessel, placed in a bath, the temperature of the calorimeter being measured by means of thermo-couples. The substance to be investigated was heated or cooled to a known temperature, and introduced into the calorimeter, the change in temperature of which was observed. Knowing the heat capacity of the calorimeter, the specific heat of the substance could be obtained. This method worked admirably, but of course it is limited to the determination of *mean* values of C_v, holding over a considerable temperature range. For the purposes in view, it was necessary, however, to be able to determine C_v for small temperature ranges, that is for a consecutive series of "points" on the temperature scale. To accomplish this, a different procedure had to be adopted.

The principle of this second method consists briefly in making the investigated substance itself act as its own calorimeter. The substance could be heated electrically by means of a platinum spiral, through which a known quantity of electrical energy was passed, as measured by an ammeter and voltmeter in the circuit. The rise in temperature of the substance was obtained by using the heating spiral itself as a resistance thermometer, *i.e.* its resistance was observed by means of a bridge, before and after the heating of the substance, the alteration in resistance giving the temperature change. Knowing the mass of substance employed, the electrical energy supplied, and the rise in temperature, it is easy to calculate the specific heat of the substance. This extremely ingenious method was worked out by Eucken, in Nernst's laboratory (*Physik. Zeitschr.*, **10**, 586, 1909), and has been employed by Nernst and his collaborators for the accurate determination of specific heats of substances at various temperatures, extending over a wide range, even down to the temperature of liquid hydrogen. A few details may be given here. A pear-shaped vessel of glass (shown in the accompanying figure, Fig. 6) contains the calorimeter K suspended by the

wires which are connected to the heating spiral. By means of a Gaede pump, together with a vessel of charcoal cooled in liquid air, a very good vacuum is maintained in the glass vessel, so as to prevent any loss of heat by convection. The calorimeter K (*i.e.* the substance itself), together with the connecting wires, is brought to a certain temperature, which is rapidly brought about by substituting hydrogen gas in place of air (since the hydrogen conducts thermally so much better). The hydrogen is subsequently removed, the vessel being evacuated. The spiral resistance is of purest platinum. Its change in resistance with temperature was calibrated by comparison with an oxygen gas thermometer. The calorimeter K varied in construction, according as to whether the substance investigated conducted heat well or badly. The first type shown in the figure is suitable when the substance is a metal.

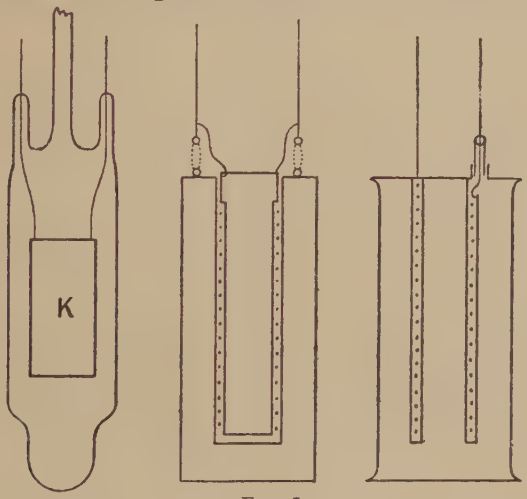

FIG. 6.

It consists of a small cylinder of the metal, having a cylindrical hole drilled almost throughout its length. Into this a plug of the same metal fits loosely, the heating spiral occupying the space between. To insulate the spiral thin paraffined paper was employed, liquid paraffin itself being finally poured in. The upper part of the plug is somewhat thicker than the remainder, good thermal contact being thus obtained. For substances which conduct heat badly the second form of calorimeter was employed. A vessel of silver was used, the platinum spiral being wound round a cylindrical sheet of silver, which served to spread the heat rapidly. Electrical insulation of the spiral was maintained by the help of shellac and thin silk. The platinum wire, on entering the calorimeter, passes through a small insulating tube, and finally, after passing through the body of the calorimeter, ends on the silver vessel, to which a lead is attached. It was found that some air must be left in the calorimeter itself (not in the pear-shaped vessel), so as to ensure

better thermal conduction, and attainment of equilibrium. Nernst also describes a third form of calorimeter, suitable for liquids, details of which will be found in the paper cited. The heat capacity of the fittings of the calorimeter K—other than the actual substance examined—was determined, and found to agree well with that calculated from the known masses and specific heats of the substances employed. When the pear-shaped vessel was well evacuated, the temperature of the substance, *i.e.* the calorimeter K (as measured by the resistance of the spiral) was found to remain remarkably constant for a considerable time, even when K had been previously cooled down to very low temperatures, by placing the non-evacuated pear-shaped vessel in contact with liquid air. Similarly, after cutting off the current the new (final) temperature was again found to remain constant, and be accurately measurable. Nernst considers that the probable error in the results does not exceed 1 per cent., and may be much less.

Some of the experimental data, obtained by the above means, have already been given in dealing with Nernst's heat theorem, and other examples will be given when we take up in greater detail the question of the applicability of Einstein's expression to the atomic heat of solids in general.

Methods of Determining the Characteristic Vibration Frequency of a Solid.

First Method.

This depends on the direct measurement of the "Reststrahlen (Residual Rays)". Many substances possess the property of selective reflection, that is they powerfully reflect rays of certain wave-length. The rays which are most strongly reflected in the case of *incident* light are those which are most strongly absorbed when the light is *transmitted*. The wave-lengths strongly absorbed are identical with the characteristic wave-lengths corresponding to the natural vibration frequencies of the substance, for it is when the light has the same frequency as that of the vibrating atom that it is most strongly absorbed. If a beam of incident light of all wave-lengths, that is to say, a beam emitted by a heated black body, is reflected successively from a number of pieces of the solid in question, at each reflection the beam will become purer, that is the reflected light tends more and more to consist of the vibration frequency characteristic of the solid. The rays which survive after having suffered a number of such reflections are called the "Residual Rays". The measurement of the wave-length and the energy of such Reststrahlen has been principally carried out by Prof. Rubens of Berlin and his collaborators, although the idea was that of Beckmann in the first instance (*cf.* Rubens and Nichols, *Annalen der Physik*, **60**, 418, 1897; Rubens and Aschkinass, *ibid.*, **65**, 241, 1898; Rubens, *ibid.*, **69**, 576, 1899; Rubens and Kurlbaum, *ibid.*, [4], **4**, 649, 1901; Rubens and Hollnagel, *Phil. Mag.*, [6], **19**, 761, 1910). These rays correspond-

ing to the vibration frequency of atoms are naturally far in the infra-red region. The apparatus employed is shown diagrammatically in the figure (Fig. 7). L is the electrically heated black body emitting waves of all frequencies. D_1 and D_2 are diaphragms of small aperture. S is a screen. The diaphragms and screen are kept cool with water at room temperature. The substance under examination is represented by P_1, P_2, P_3, P_4. The surfaces of these pieces are polished as highly as possible. M is an adjustable mirror and T the thermopile. A diffraction grating of special make could be inserted in the path of the beam, thereby analysing it into a spectrum, the position of the energy maxima corresponding to the characteristic vibration frequencies of the substance P being determined by means of the thermopile. In later experiments the grating had to be abandoned owing to the large amount of absorp-

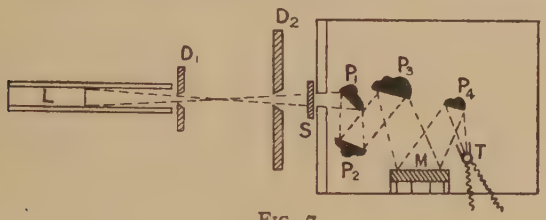

FIG. 7.

tion suffered by the rays in passing through it. Instead, an interference method has been devised—see the paper by Rubens and Hollnagel, *Phil. Mag.*, *l.c.* The following table contains some of the results summarised by Rubens and von Wartenberg (*Sitzungsber. königl. preuss. Akad.*, 1914, p. 169). In actual experiment two bands are usually observed fairly close together. One of these, however, is due to the presence of water vapour (Rubens, *ibid.*, 1913, p. 513).

RESIDUAL RAYS CHARACTERISTIC OF CERTAIN SOLID SALTS.

Substance.	Wave-Length in μ.	Substance.	Wave-Length in μ.
NH_4Cl . .	51·5	AgCN . .	93 approx.
NaCl . .	52·0	KI . . .	94·1
NH_4Br . .	59·3	$HgCl_2$ . .	95 approx.
KCl . .	63·4	$CaCO_3$ . .	98·7
AgCl . .	81·5	Hg_2Cl_2 . .	98·8
KBr . .	82·6	AgBr . .	112·7
$PbCl_2$ . .	91·0	TlBr . .	117·0
TlCl . .	91·6	TlI . .	151·8

Second Method.

This is an indirect method due to Einstein (*Annalen d. Physik*, [4], **34**, 170, 1911). From consideration of the distribution of atoms in metals and the forces acting upon them when they are displaced from their centres of gravity during vibration, Einstein obtained an approximate

expression for the characteristic vibration frequency ν in terms of the compressibility K, the atomic (or molecular) volume V, and the atomic (or molecular) weight M, which may be written as follows:—

$$\nu = 2{\cdot}54 \times 10^7 \frac{V^{\frac{1}{3}}}{M^{\frac{1}{2}}K^{\frac{1}{2}}}.$$

Using Grüneisen's recent data for the compressibility (*Ann. der. Physik*, **25**, 848, 1908), Einstein calculated the following characteristic vibration frequencies:—

SOME OF EINSTEIN'S VALUES FOR ν.

Substance.	ν.	Substance.	ν.
Al . .	$6{\cdot}6 \times 10^{12}$	Fe . .	$6{\cdot}5$
Cu . .	$5{\cdot}7$	Pt . .	$4{\cdot}6$
Ag . .	$4{\cdot}1$	Pb . .	$2{\cdot}2$
Au . .	$3{\cdot}8$	Cd . .	$2{\cdot}6$
Ni . .	$6{\cdot}6$	Bi . .	$1{\cdot}8$

Einstein himself does not claim that this method is more than a rough approximation. Nevertheless the values agree moderately well with those obtained by other methods.

Third Method.

This method, also an indirect one, is due to F. A. Lindemann (*Physikal. Zeitsch.*, **11**, 609, 1910). It is based upon the assumption that *at the melting point* T_s *of a solid the amplitude of vibration of the atoms is approximately equal to the mean distance of the atoms apart.* Let us denote by r_s the radius of the circular vibration of an atom (in a metal, say), then the mean velocity u with which it vibrates is given by $u = 2\pi r_s \nu$, where ν is, of course, the number of such vibrations per second.

The mean kinetic energy of vibration is $\frac{1}{2}mu^2$, where m is the mass of the atom, and since there is likewise present an equal quantity of potential energy, the total mean energy of a vibrating atom is mu^2 or $4m\pi^2 r_s^2 \nu^2$. Now at the melting point the metals may be considered as very closely obeying Dulong and Petit's Law, *i.e.* their atomic heat is practically 6. That is, the expression for the vibrating energy which is given by—

$$U = \frac{3R}{N} \times \frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1} \text{ reduces to } \frac{3RT_s}{N}$$

for large values of T as already pointed out.

Hence $$4\pi^2 m r_s^2 \nu^2 = \frac{3RT_s}{N},$$

or $$\nu \propto \sqrt{\frac{T_s}{m r_s^2}}.$$

If we now regard the atomic volume V as proportional to the cube of the mean distance apart of the atoms (which distance is identical with r_s on Lindemann's assumption), we can write—

$$\nu \propto \sqrt{\frac{T_s}{mV^{2/3}}}.$$

The proportionality factor obtained by comparison with experiment is $2{\cdot}80 \times 10^{12}$, and hence Lindemann's formula is—

$$\nu = 2{\cdot}80 \times 10^{12} \sqrt{\frac{T_s}{mV^{2/3}}}.$$

It is thus possible to calculate ν from measurements of melting temperature, molecular weight of the atoms, and the atomic volume. This is an extremely convenient method, but has the disadvantage of not giving ν very accurately. It appears, however, to be somewhat more accurate than Einstein's method (Method 2). The following table is given by Nernst and Lindemann (*Z. Elektrochem.*, **17**, 822, 1911). The observed values of ν are those given by a formula of Nernst and Lindemann which is a modification of Einstein's expression for atomic heat, which at the same time represents experimental values more closely. We shall discuss this expression later, but in the meantime it may be taken as giving the values of ν from atomic heat measurements.

LINDEMANN'S FORMULA FOR "ν".

Substance.	Molecular Weight.	T_s Melting Point.	V Molecular Volume.	ν Calculated by Lindemann's Formula.	ν "Observed".
Al . .	23·1	930	10·0	$7{\cdot}6 \times 10^{12}$	$8{\cdot}3 \times 10^{12}$
Cu . .	63·6	1357	7·1	6·8	6·6
Zn . .	65·4	692	9·2	4·4	4·8
Ag . .	107·9	1234	10·3	4·4	4·5
Pb . .	206·9	600	18·3	1·8	1·9
Diamond .	12·0	3600 ?	3·4	32·5	40·0
Iodine .	127·0	386	25·7	1·7	2·0
NaCl . .	29·2	1083	13·5	7·2	5·9
KCl . .	37·2	1051	18·9	5·6	4·5

Lindemann's formula, like Einstein's, gives only a single *mean* characteristic vibration frequency. For this purpose, therefore, the molecule of NaCl, KCl, etc., is treated as a single atom having an atomic weight one-half of that usually assigned to the *molecule* of these substances.

Fourth Method.

This method has also been suggested by Lindemann (*Ber. Deutsch. phys. Ges.*, **13**, 1107, (1911)). Lindemann has shown (*ibid.*, p. 482) that the characteristic ultra-violet frequency ν which enters into the selective photo-electric effect[1] is given by the expression—

[1] *Cf.* Chap. VI.

$$\nu_{\text{violet}} = \frac{1}{2\pi}\sqrt{\frac{ne^2}{mr^3}}$$

where n is the "valency," e the charge on an electron (in electostatic units), m the mass of an electron, and r one half of the distance between the centres of two neighbouring atoms.

Lindemann introduces an expression due to Haber and discussed later (p. 133), which connects the ultra-violet frequency with the characteristic infra-red frequency, ν_{red}, the relation being—

$$\frac{\nu_{\text{violet}}}{\nu_{\text{red}}} = \sqrt{\frac{\text{M}}{m}}$$

where m is the mass of an electron, and M the actual mass of the atom. Combining this expression with that given above we obtain—

$$\nu_{\text{red}} = \frac{e}{2\pi}\sqrt{\frac{n}{\text{M}r^3}}.$$

Further, if A is the atomic weight, N the number of atoms in one gram-atom, and d the density of the substance, then Lindemann shows that—

$$r = \frac{\sqrt[6]{2}}{2} \cdot \sqrt[3]{\frac{\text{A}}{d \cdot \text{N}}}.$$

Hence,

$$\nu_{\text{red}} = \frac{\sqrt[4]{2}}{\pi} \cdot e \cdot \text{N} \cdot \frac{\sqrt{dn}}{\text{A}}.$$

But $e\text{N} = \text{F} =$ the Faraday $= 2{\cdot}9 \times 10^{14}$ electrostatic units.

Hence,

$$\nu_{\text{red}} = 1{\cdot}095 \times 10^{14}\frac{\sqrt{d \cdot n}}{\text{A}}.$$

By means of a suitable choice of n we can calculate the infra-red frequency of an element from this formula. The calculated values agree with those observed, in some cases better than do those values obtained by the melting point method. There is a certain arbitrariness, however, in the choice of the valency n, as will be seen from the following table which is quoted from Lindemann's paper :—

Element.	n.	Lindemann Melting-point Formula.	$1{\cdot}1 \times 10^{14}\frac{\sqrt{n \cdot d}}{\text{A}}$.	ν "Observed".
Al . . .	1	$7{\cdot}6 \times 10^{12}$	$8{\cdot}2 \times 10^{12}$	$8{\cdot}3 \times 10^{12}$
Cu . . .	2	6·8	7·2	6·6
Ag . . .	2	4·4	4·6	4·4
Hg . . .	1	1·3	2·0	2·2
Pb . . .	2	1·8	2·5	1·9
Diamond . .	4	>32·5	34·1	40·0
S . . .	2	3·9	6·6	7·3
I . . .	1	1·7	1·9	2·0

The weakness of the method lies in the selection of the value of the valency n of the element under consideration. Of the four methods mentioned, Lindemann's melting-point method is probably the most

convenient; the most accurate method is undoubtedly the direct measurement of the frequency of the residual rays.

The System of Elements and the Periodicity of the Vibration Frequency with the Atomic Weights.

(*Cf.* W. Biltz, *Zeitsch. Elektrochem.*, **17**, 676, 1911.)

Employing Lindemann's formula, Biltz has calculated the characteristic vibration frequency ν for the elements (in the solid state) as far as the existing data upon melting point and density permitted, and has traced out a relation between the frequency and the atomic weight. In the following table are given the values of ν for each element as calculated by the help of Lindemann's formula[1]:—

Element.	Density.	Melting-point Temperature T Absolute.	Atomic Weight.	$\nu \times 10^{-12}$.
H . . .	0·0763	14	1·01	4·36
He (liquid) .	0·154	*Ca* 2	3·99	0·66
Li . . .	0·59	459	6·94	10·0
Be . . .	1·73	*Ca* 1200	9·1	18·5
C (graphite) .	2·3	,, 3600	12·0	27·7
C (diamond) .	3·52	,, 3600	12·0	31·7
N . . .	1·03	62·5	14·0	2·5
O . . .	1·43	28	16·0	1·7
F (liquid) . .	1·14	50	19·0	1·8
[Ne (liquid) .	1·24	*Ca* 2	20·2	0·34
Na . . .	0·98	371	23·0	3·96
Mg . . .	1·74	924	24·3	7·2
Al . . .	2·66	930	27·1	7·5
Si . . .	2·49	1700	28·3	9·6
P (red) . .	2·34	903	31·0	6·3
S (rhombic) .	2·07	388	32·1	3·95
Cl (liquid) .	1·66	171	35·5	2·24
Ar (liquid) .	1·42	85	39·9	1·32
K . . .	0·87	335	39·1	2·3
Ca . . .	1·59	1050	40·1	4·9
Ti . . .	4·50	2120	48·1	8·4
Vd . . .	5·8	1950	51·1	8·3
Cr . . .	6·74	1790	52·0	8·3
Mn . . .	7·39	1520	54·9	7·5
Fe . . .	7·85	1820	55·9	8·3
Co . . .	8·72	1780	59·0	8·2
Ni . . .	8·90	1760	58·7	8·2
Cu . . .	8·93	1357	63·6	6·7
Zn . . .	7·12	692	65·4	4·36
Ga . . .	5·95	303	69·9	2·5
Ge . . .	5·47	*Ca* 1100	72·5	4·6
As . . .	5·73	,, 1000	75·0	4·36
Se (grey) . .	4·8	490	79·2	2·7
Br (liquid) .	3·19	266	79·9	1·7
Kr (liquid) .	2·16	104	82·9	0·9
Rb . . .	1·52	311	85·5	1·45
Sr . . .	2·63	[1080]	87·6	3·0

[1] The values of ν are slightly different from those given by Biltz, as Biltz employed the older and less correct proportionality factor $2{\cdot}12 \times 10^{12}$ in Lindemann's formula instead of the later one, $2{\cdot}80 \times 10^{12}$.

Element.	Density.	Melting-point Temperature T Absolute.	Atomic Weight.	$\nu \times 10^{-13}$.
[Zr . .	6·4	*Ca* 2700	90·6	—
[Nb . .	7·8	2220	93·5	—
Mo . .	9·01	2400	96·0	6·3
[Ru . .	12·3	*Ca* 2250	102·0	—
Pd . . .	11·9	1860	107·0	5·74
Ag . .	10·5	1234	108·0	4·36
Cd . . .	8·65	595	112·0	3·0
In . . .	7·12	428	115·0	2·1
Sn . . .	7·30	505	119·0	2·24
Sb . . .	6·62	904	120·0	3·0
Te . . .	6·23	723	127·5	2·45
I . . .	4·66	386	127·0	1·6
X (liquid) .	3·52	133	130·0	0·85
Cs . . .	1·89	299	133·0	0·95
Ba . . .	3·78	1120	137·0	2·4
La . . .	6·16	1085	139·0	2·8
Ce . . .	7·04	896	140·2	2·64
Ta . . .	16·6	2575	181	4·75
Os . . .	22·5	2700	191	5·1
Ir . . .	22·4	2500	193	4·9
Pt . . .	22·5	2018	195	4·36
Au . . .	19·3	1337	197	3·4
Hg . .	14·2	234	200	1·25
Tl . . .	11·8	575	204	1·84
Pb . . .	11·4	600	207	1·84
Bi . . .	9·78	541	208	1·6
[Th . .	12·2	*Ca* 2100	232	3·2]

Biltz points out that in the characteristic frequency we have a very fundamental atomic constant. Further, since its measurement involves *two* properties, namely, specific volume and melting point, it is a step further than the stage reached, for example, in Lothar Meyer's curve, in which one property only is brought into relation to the atomic weight. Some doubt, of course, exists regarding the values in the case of a few elements, especially those possessing allotropic forms. Biltz has plotted the frequencies against the atomic weights, and has found the periodic variation shown in the figure (Fig. 8). It will be seen to be quite analogous to Mendeleef's original scheme. The majority of the elements occupy places on the curve, exceptions being fluorine, manganese, tin, and tellurium. Argon and potassium occupy as usual their anomalous position. The position of hydrogen, which was for a long time in doubt, is clearly that of the first member of the halogen series, as Ramsay had insisted on many years ago. The unique position of carbon, with extremely high value of ν, brings out very clearly its unique chemical character as regards its immense capability of forming compounds. An atom possessing high frequency no doubt is the most likely type of atom to allow of the transfer of electrons to and from itself, *i.e.* valency electrons.

Further Consideration of Einstein's Expression for Atomic Heat.

Einstein's expression, *viz.*—

$$C_v = 3R \frac{e^{\beta_0 \nu/T} \left(\frac{\beta_0 \nu}{T}\right)^2}{\left(e^{\beta_0 \nu/T} - 1\right)^2}$$

has been applied to several metals and solid salts. The following two

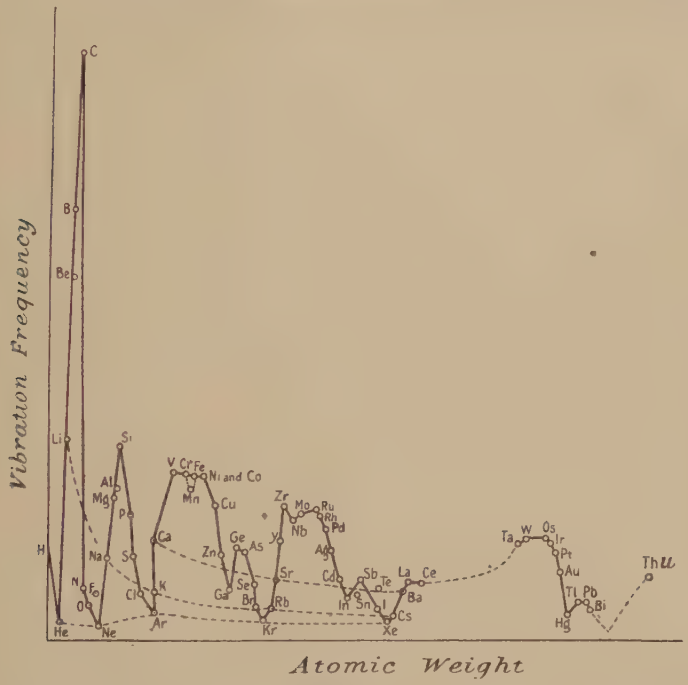

FIG. 8.

examples, at low temperatures, given by Nernst and Lindemann (*Zeitsch. Elektrochem.*, **17**, 818, 1911), are instructive :—

COPPER. $\beta_0 \nu = 240$.

Temperature, Absolute.	Atomic Heat (Observed).	Atomic Heat (Calculated).
86·0	3·38	3·31
33·4	0·538	0·234
22·5	0·223	0·023

POTASSIUM CHLORIDE. $\beta_0\nu = 218$.

Temperature, Absolute.	Atomic Heat (Observed).	Atomic Heat (Calculated).
86·0	4·36	3·54
52·8	2·80	1·70
30·1	0·98	0·235
22·8	0·58	0·039

It is clear that while Einstein's formula gives the qualitative course of the variation of C_v with temperature, it is far from reproducing the variation quantitatively. It might be thought that this is due to an error in using a single frequency value where in the actual case there might be a broad band. From Rubens' results already quoted it will be seen, however, that the characteristic frequency of each salt is fairly isolated, and at lower temperatures this isolation would become still more perfect. In metallic elements themselves, where it is usually regarded that we are dealing with uncombined (unpolymerised) atoms themselves, the characteristic frequency should be quite sharp and well defined.

As a way out of the difficulty—prior to the publication of Debye's formula of 1912, to which reference will be made later—Nernst and Lindemann proposed an empirical expression for C_v, which differs somewhat from that of Einstein.

The Nernst-Lindemann Formula for the Atomic Heat of Solids.

This expression takes the following form :—

$$C_v = \tfrac{3}{2}R\left\{\frac{\left(\frac{\beta_0\nu}{T}\right)^2 . e^{\beta_0\nu/T}}{(e^{\beta_0\nu/T} - 1)^2} + \frac{\left(\frac{\beta_0\nu}{2T}\right)^2 . e^{\beta_0\nu/2T}}{(e^{\beta_0\nu/2T} - 1)^2}\right\} . \quad . \quad (1)$$

that is, the atomic heat expression of Einstein has been split up into two portions. One portion represents the energy corresponding to the characteristic frequency ν; the second portion represents the energy due to the harmonic vibration, which is one "octave" lower than the characteristic, namely, $\frac{\nu}{2}$. Why this "octave" should be introduced is as yet practically unexplained. The expression, however, reproduces the experimental value of C_v with extraordinary accuracy. Its importance is therefore not to be questioned. Some illustration of its applicability may be given here.

First of all, we have to notice that the direct experimentally determined values of the atomic heat, such as those of Nernst and his collaborators, hold for constant pressure, *i.e.* they are (C_p) values. In the formula, however, it is the atomic heat at constant volume, *viz.* C_v, which occurs. They are nearly identical, but not quite. We have,

therefore, to convert the one into the other. The procedure is as follows. On the basis of thermodynamics [1] we have the relation—

$$C_p = C_v\left(1 + \frac{9T\alpha^2V}{KC_v}\right)$$

where α is the linear coefficient of expansion, V the molecular or atomic volume, and K the compressibility. Now experiment has shown that it is allowable to consider $\frac{V}{K}$ as a constant, independent of T (especially as it occurs in a small correction term), and further, making use of Gruneisen's relation (*Verhand. d. d. physik. Gesell.*, 1911, 491) regarding the proportionality between C_p and the expansion coefficient α, we can rewrite the above expression in the form—

$$C_p = C_v + C_p^2TA\,*$$

where A is a constant characteristic of each substance. The values of A are given in the following table for some metals and salts :—

VALUES OF THE CONSTANT "A".

Substance.	Atomic Volume V.	$3\alpha \times 10^6$.	$K \times 10^{12}$.	C_p/C_v.	$A \times \pi 0^5$.
Al . .	10·0	72	1·48	1·042	2·2
Cu . .	7·1	48	0·785	1·025	1·3
Ag . .	10·3	55	0·775	1·047	2·5
Pb . .	18·3	82	2·4	1·055	3·0
Pt . .	9·1	27	0·40	1·019	1·0
NaCl . .	13·5	121	4·28	1·051	2·7
KCl . .	18·9	114	7·6	1·038	2·0

In the case of substances for which the compressibility K and the coefficient of expansion α are known, it is easy to convert C_v values into C_p, or *vice versâ*. For other substances, however, the procedure is somewhat different. The individual constant A can be shown to be inversely proportional to the melting point T_s (*cf.* Nernst and Lindemann, *loc. cit.*). We can thus write $A = \frac{A_0}{T_s}$ where A_0 is a universal constant having the value 0·0214 (C.G.S. units). Hence—

$$C_p = C_v + C_p^2\frac{T}{T_s}A_0.$$

[1] G. N. Lewis, *J. Amer. Chem. Soc.*, **29**, 1165 (1907).

* This expression has been recently transformed into a still simpler one, *viz.* $C_p = C_v + \alpha T^{3/2}$, where α is an empiric constant characteristic of the substance in question (Lindemann and Magnus, *Z. Elektroc em.*, **16**, 269, 1910; *cf.* also Nernst, *Ann. Physik*, **36**, 395, 1911). Since direct measurement always gives us C_p, this is a very convenient way of getting C_v.

The general method adopted by Nernst and Lindemann to test their formula, equation 1, was, first of all, to calculate C_v by its means for substances for which ν is known (either by means of Reststrahlen measurements, or by means of Lindemann's melting-point formula). The "calculated" value of C_v was then converted into terms of C_p by means of the expression—

$$C_p = C_v + C_p^2 TA$$

and the result finally compared with the observed values of C_p.

The following tables give the results obtained in the case of aluminium, copper, silver, lead, and the salts KCl, NaCl, KBr, and the diamond. These are all taken from the paper of Nernst and Lindemann (*loc. cit.*) :—

ALUMINIUM. $\beta_0\nu = 405$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
32·4	0·23	0·23	0·25	Nernst.
35·1	0·31	0·31	0·33	,,
83·0	2·42	2·43	2·41	,,
86·0	2·52	2·53	2·52	,,
88·3	2·61	2·62	2·62	,,
137·0	3·99	4·05	3·97	Koref.
235·0	5·15	5·30	5·32	Koref, Schimpff.
331·0	5·52	5·76	5·82	Magnus, Schimpff.
433·0	5·70	6·06	6·10	Magnus.
555·0	5·80	6·30	6·48	,,

COPPER. $\beta_0\nu = 321$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
23·5	0·15	0·15	0·22	Nernst.
27·7	0·31	0·31	0·32	,,
33·4	0·59	0·59	0·54	,,
87·0	3·35	3·37	3·33	,,
88·0	3·37	3·39	3·38	,,
137·0	4·60	4·65	4·57	Koref.
234·0	5·42	5·52	5·59	Koref, Schimpff.
290·0	5·60	5·75	5·79	Gaede.
323·0	5·66	5·81	5·90	Bartoli, Stracciati, Schimpff.
450·0	5·81	6·03	6·09	Magnus.

SILVER. $\beta_0\nu = 221$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
35·0	1·59	1·59	1·58	Nernst.
39·1	1·92	1·92	1·90	,,
42·9	2·22	2·22	2·26	,,
45·5	2·43	2·44	2·47	,,
51·4	2·81	2·82	2·81	,,
53·8	2·97	2·98	2·90	,,
77·0	4·07	4·11	4·07	,,
100·0	4·72	4·77	4·86	Koref.
200·0	5·60	5·77	5·78	,,
273·0	5·77	6·02	6·00	Koref, Schimpff.
331·0	5·82	6·12	6·01	Bartoli, Stracciati, Sc impff.
535·0	5·90	6·45	6·46	Magnus.
589·0	5·92	6·57	6·64	,,

LEAD. $\beta_0\nu = 95$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
23·0	2·95	2·96	2·96	Nernst.
28·3	3·63	3·64	3·92	,,
36·8	4·35	4·37	4·40	,,
38·1	4·43	4·45	4·45	,,
85·5	5·60	5·68	5·65	,,
90·2	5·62	5·70	5·71	,,
200·0	5·90	6·12	6·13	Koref.
273·0	5·92	6·24	6·31	Koref, Gaede.
290·0	5·92	6·26	6·33	Gaede.
332·0	5·93	6·31	6·41	Magnus, Schimpff.
409·0	5·94	6·40	6·61	Magnus.

ATOMIC HEAT OF DIAMOND.

$\beta_0\nu = 1940$ (obtained by using Lindemann's formula, the melting point being taken as 3600°).

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
30	0·000	0·000	0·00	Nernst.
42	0·000	0·000	0·00	,,
88	0·006	0·006	0·03	,,
92	0·009	0·009	0·03	,,
205	0·62	0·62	0·62	,,
209	0·65	0·65	0·66	,,
220	0·74	0·74	0·72	,,
222	0·78	0·78	0·76	Weber.
232	0·87	0·87	0·86	Koref.
243	0·97	0·97	0·95	Dewar.
262	1·16	1·16	1·14	Weber.
284	1·37	1·37	1·35	,,
306	1·59	1·59	1·58	,,
331	1·82	1·83	1·84	,,
358	2·07	2·08	2·12	,,
413	2·53	2·55	2·66	,,
1169	5·19	5·41	5·45	,,

The agreement between theoretical and observed values is good. The important point about the diamond, as already remarked, is that it ceases to have any measurable heat capacity at all for about 40° above absolute zero. This is in agreement both with the thermodynamic theorem of Nernst and the Einstein theory of specific heat.

We now pass to the consideration of the salts KCl, NaCl, and KBr. Each of these possesses a single well-defined band in the far infra red measured experimentally by Rubens. This value has been employed in the equation. The values of C_v and C_p are mean atomic heats, *i.e.* one half the molecular heats.

KCl. $\beta_0\nu = 218$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
22·8	0·61	0·61	0·58	Nernst
26·9	0· 0	0·70	0·76	,,
30·1	1·23	1·23	0·98 ?	,,
33·7	1·53	1·53	1·25 ?	,,
39·0	1·98	1·98	1·83	,,
48·3	2·66	2·66	2·85	,,
52·8	2· 6	2·97	2·80	,,
57·6	3·25	3·26	3·06	,,
63·2	3·57	3·59	3·36	,,
70·0	3·85	3·87	3·79	,,
76·6	4·10	4·13	4·11	,,
86·0	4·40	4·43	4·36	,,
137·0	5·26	5·33	5·25	Koref
2 5·0	5·70	5·86	5·89	,,
331·0	5·83	6·06	6·16	Magnus
416·0	5·87	6·21	6·36	,,
550·0	5·91	6·36	6·54	,,

NaCl. $\beta_0\nu = 287$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
25·0	0·32	0·32	0·29	Nernst
25·5	0·34	0·34	0·31	,,
28·0	0 48	0·48	0·40	,,
67·5	2·87	2·88	3·06	,,
69·0	2·94	2·95	3·13	,,
81·4	3·47	3·49	3·54	,,
83·4	3·61	3·64	3·75	,,
138·0	4·82	4·90	4·87	Koref
235·0	5·52	5·73	5·76	,,

KBr. $\beta_0\nu = 177$ (C_p was calculated from C_v by the usual formula, the value of A being taken as identical with that for NaCl).

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
78·7	4·67	4·70	4·74	Nernst
82·5	4·77	4·80	4·76	,,
85·4	4·82	4·85	4·82	,,
89·2	4·91	4·94	5·03	,,
137·0	5·47	5·56	5·42	Koref
234·0	5·79	6·02	6·10	,,

The agreement between the observed mean atomic heat of these three salts and that calculated on the basis of the Nernst-Lindemann equation would appear to be thoroughly satisfactory. This, however, is really to a large extent accidental. Nernst found later that the Nernst-Lindemann equation would not apply to other salts. He was led ultimately to a different treatment of the problem of the mean atomic heat (or half molecular heat) of polyatomic substances which will be discussed briefly when we have become acquainted with the equation of Debye.

It should be pointed out that no very clear theoretical significance can be attached to the Nernst-Lindemann equation even when applied to monatomic substances. Its merit is that it reproduces experimental data in such cases with a high degree of accuracy, and in this respect is decidedly to be preferred to the equation of Einstein. The Nernst-Lindemann equation resembles Einstein's in that a single frequency ν, obtained by one of the methods mentioned previously, is employed, along with one half of this quantity.

The Specific Heat of Solids at High Temperatures and the Significance of the Energy possessed by the Electrons.

It will be remembered that the expression for the atomic heat (at constant volume) of a solid, whether stated in the original form of Einstein or in the Nernst-Lindemann modification, reaches as a limit the value 3R (5·95 cals.). As a matter of fact, however, the atomic heat (at *constant volume*) has been found to exceed this limit considerably when the temperature to which the value of the atomic heat refers is very high. At these temperatures there must be some other source of internal energy content not taken account of in simply ascribing the total energy to the vibrations of the *atoms*. At high temperatures the body becomes "white hot," that is it is capable of emitting short waves in the *visible*, which are due in all probability (as we have already seen) to the vibrations of the *electrons* in the atoms. Although the energy of the electrons can be neglected at low temperatures compared with that possessed by the atoms, this is no longer the case at high temperatures, and hence such must be taken into account in any expression

for specific (or atomic) heat. An attempt in this direction has been made by J. Koenigsberger (*Zeitsch. Elektrochem.*, **17**, 289, 1911), who considers that the atomic heat of metals (at constant volume) should reach 9 instead of 6, by taking the vibrating energy of the electrons into account. No great stress, however, can be laid upon the significance of the actual numerical limit quoted (*cf.* Nernst and Lindemann, *loc. cit.*). It is interesting, however, to see the numerical values for the atomic heat C_v actually obtained at high temperatures (*cf.* Koenigsberger, *loc. cit.*) :—

ATOMIC HEAT (AT CONSTANT VOLUME) AT HIGH TEMPERATURES.

Metal.	Region of Temperature.	C_v.	Observer.
Silver . . .	907-1100° C.	6·7	Pionchon (1887).
Tin	1100°	9·2	,,
Iron . . .	1200°	9·6	,,
Nickel . . .	1150°	7·9	,,
Copper . . .	900°	7·1	Richards (1893).
Aluminium . .	650°	7·7	Boutchew.

DEBYE'S EQUATION FOR THE ATOMIC HEAT OF SOLIDS.

(P. Debye, *Ann. Physik*, [iv.], **39**, 789, 1912.)

We have seen that Einstein's specific (atomic) heat formula only holds qualitatively, and that whilst that of Nernst and Lindemann accords much better with experiment, their expression suffers from the very serious drawback of lacking a sound theoretical basis. Debye has recently developed an expression having a theoretical basis—employing the quantum hypothesis—and has found that the expression reproduces experimental values with even greater fidelity than that of Nernst and Lindemann. Debye's formula may therefore be regarded as the most significant of all specific heat formulæ yet proposed. The general line of thought pursued by Debye is as follows :—[1]

In Einstein's investigation it was assumed for the sake of simplicity that the vibrating particle (the atom) only gave rise to monochromatic radiation (frequency ν) and only absorbed such. Instead of this limitation to a single characteristic frequency ν, Debye works out the expression for atomic heat on the basis of absorption (and emission) of a number of vibration frequencies, in fact a whole spectrum. It will be seen at once that this is far more likely to coincide with what actually occurs than the simpler assumption of Einstein. Debye starts out with the very plausible assumption that a vibrating atom in a solid cannot be vibrating simply harmonically with a *single* frequency, but owing to the proximity of other atoms and probably to collisions with them the

[1] For details see Debye's paper. Also Appendix II.

mode of vibration will be complex. Such complex modes of vibration can be treated, as Fourier showed, as theoretically made up of a *series* of true simple harmonic motions, and we have thus to integrate over a spectrum of frequencies if we wish to calculate with greater exactness the total energy content of a vibrating atom. The first point to be noted is, however, that we do *not* deal with a spectrum extending from $\nu = 0$ to $\nu = \infty$. If a body consists of N atoms—treated as massive points—the system possesses 3N degrees of freedom. The system will therefore in general exercise 3N different periodic vibrations, *i.e.* 3N different vibration frequencies. If the older view—consonant with the principle of *equi*partition of energy—were true, namely, that the energy was the same for each degree of freedom over the entire spectrum, then we could state directly that each vibration frequency corresponded to the energy kT (where $k = \frac{R}{N}$, N being now the number of atoms in 1 gram-atom), so that the total energy of the body would be simply 3NRT per gram-atom as Dulong and Petit's Law requires.

We have seen, however, that the whole point of the quantum theory is the negation of the principle of equipartition throughout a spectrum, and that instead the energy per vibration varies with the type of vibration. This lack of equipartition is expressed as we have already seen in the Planck expression $\frac{h\nu}{e^{h\nu/kT} - 1}$, which gives the true mean energy of any single vibration ν. To obtain the total energy of the vibrating system it is necessary to sum this expression over the spectrum (of absorption or emission), the spectrum not containing an infinite number of frequencies but limited to 3N, as already pointed out. The spectrum is characterised by two factors, (*a*) its boundaries, (*b*) the density of the lines, *i.e.* the number of lines in any given vibration region $d\nu$. There is, according to Debye, a certain definite limiting frequency ν_m beyond which the spectrum does not extend. Debye has reached a number of important conclusions in the course of his investigation. The first is this: *If the temperature* T *be regarded as a multiple* (*or submultiple*) *of a temperature* θ (*a characteristic constant for any given substance*), *then the atomic heat for all monatomic substances can be represented by the same curve*, i.e. *the atomic heat is a universal function of* $\frac{T}{\theta}$.

A second relation which is not confined to monatomic substances states that *the number of lines spread over a region* $d\nu$ *is proportional to* $\nu^2 d\nu$ (a relation for black-body radiation already obtained by Jeans). From this Debye concludes that *at sufficiently low temperatures the atomic heat of all solids is proportional to* T^3, *that is to the third power of the absolute temperature.* This conclusion differs (theoretically) widely from the conclusion of the Einstein and the Nernst-Lindemann equations. It is borne out by the experimental data, but experiment at low

temperature bears out the Nernst-Lindemann view equally. As a corollary it follows that the *atomic energy content at low temperatures is proportional* to the fourth power of the absolute temperature (*cf.* Stefan's Law for total radiation). Debye's expression for the energy U of a solid of volume V which contains N atoms is—

$$U = \frac{9N}{\nu_m^3}\int_0^{\nu_m} \frac{h\nu}{e^{h\nu/kT} - 1} \cdot \nu^2 d\nu \quad . \quad . \quad . \quad (1)$$

the energy not being ascribed to a single harmonic vibration ν, but to a spectrum of such extending from o to ν_m. If we now define the temperature θ (the characteristic constant of the substance) by the expression—

$$\theta = \frac{h\nu_m}{k} = \beta\nu_m \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and introduce into equation (1) as a new dimensionless variable—the magnitude—

$$\xi = \frac{h\nu}{kT} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we can write—

$$U = 9NkT\left(\frac{kT}{h\nu_m}\right)^3 \int_0^{h\nu_m/kT} \frac{\xi^3 d\xi}{e^{\xi} - 1} \quad . \quad . \quad . \quad (4)$$

or, substituting θ for $\frac{h\nu_m}{k}$, we obtain—

$$U = 9NkT\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{\xi^3 d\xi}{e^{\xi} - 1} \quad . \quad . \quad . \quad (5)$$

Dulong and Petit's Law, if true, would require the relation—

$$U = 3NkT.$$

Now if we write $\frac{\theta}{T} = x$, and differentiate equation (5) with respect to temperature, we obtain finally—

$$C_v = 3Nk\left(\frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^{\xi} - 1} - \frac{3x}{e^x - 1}\right) \quad . \quad . \quad . \quad (6)$$

The magnitude $3Nk$ has the value 5·955 cals. and may be denoted by C_∞ since this numerical limit is reached at high temperatures. Equation (6) may therefore be rewritten in the form—

$$\frac{C_v}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^{\xi} - 1} - \frac{3x}{e^x - 1} \quad . \quad . \quad . \quad (7)$$

Equation (6) or (7) is Debye's atomic heat formula.

For the case in which x *is small, i.e.* T is large (compared to θ), $\frac{\xi^3}{e^\xi - 1}$ becomes ξ^2, and $\frac{3x}{e^x - 1}$ becomes $\frac{3x}{x}$ or simply 3. Hence, $\frac{C_v}{C_\infty} = \frac{12}{3} - 3 = 1$, in other words, Dulong and Petit's Law holds at high temperatures. On the other hand, when x *is large, i.e.* T is small, we obtain by expanding $\int_0^\infty \frac{\xi^3 d\xi}{e^\xi - 1}$ the series $\xi^2(e^{-\xi} + e^{-2\xi} + e^{-3\xi} + \ldots)d\xi$, or—

$$6\left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \ldots\right).$$

Hence equation (7) yields—since the series expression in the bracket is 1·0823—

$$\frac{C_v}{C_\infty} = \frac{12 \times 6 \times 1{\cdot}0823}{x^3} = 77{\cdot}938\frac{T^3}{\theta^3}.$$

That is, at sufficiently low temperatures, the atomic heat is proportional to the cube of the absolute temperature T. (The above relation can be used to calculate θ, employing the experimental value of $\frac{C_v}{C_\infty}$ at some low temperature.)

Debye has tested his formula (equation (6) or (7)) and found it to agree very well with experiment. It has further been tested independently by Nernst and Lindemann (*Sitzungsber. Berl. Akad.*, p. 1160, 1912) with the following results, in which the values of C_p (atomic heat at constant pressure) are obtained from the values of C_v given by Debye's formula by employing one of the relations between C_p and C_v mentioned at an earlier stage. Nernst and Lindemann slightly alter the form of Debye's equation (in respect of the symbols) so as to bring it more into line with previous expressions. The expression as used by them takes the form—

$$C_v = 3R\left[\frac{4\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 - \frac{3\frac{\beta\nu}{T}}{e^{\beta\nu/T} - 1} - 12\frac{\beta\nu}{T}\sum_{n=1}^{n=\infty} e^{-n\frac{\beta\nu}{T}}\left\{\frac{1}{n\frac{\beta\nu}{T}} + \frac{3}{n^2\left(\frac{\beta\nu}{T}\right)^2} + \frac{6}{n^3\left(\frac{\beta\nu}{T}\right)^3} + \frac{6}{n^4\left(\frac{\beta\nu}{T}\right)^4}\right\}\right]$$

ALUMINIUM ($\theta = \beta\nu = 398$; earlier value employed = 405).

T.	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye).	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
32·4	0·25	0·25	0·00	+ 0·02
35·1	0·33	0·32	+ 0·01	+ 0·02
83·0	2·41	2·36	+ 0·05	− 0·02
86·0	2·52	2·50	+ 0·02	− 0·01
88·3	2·62	2·59	+ 0·03	0·00
137·0	3·97	4·10	− 0·13	− 0·08
235·0	5·32	5·34	− 0·02	+ 0·02
331·0	5·82	5·78	+ 0·04	+ 0·06
433·0	6·10	6·07	+ 0·03	+ 0·04
555·0	6·48	6·30	+ 0·18	+ 0·18

DIAMOND ($\beta\nu = 1860$; earlier value 1940).

T.	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye).	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
88	0·028	0·049	− 0·021	+ 0·022
92	0·033	0·058	− 0·025	+ 0·024
205	0·618	0·61	+ 0·008	0·00
209	0·662	0·66	+ 0·002	+ 0·01
220	0·722	0·74	− 0·018	− 0·64
222	0·76	0·75	+ 0·01	− 0·02
243	0·95	0·925	+ 0·025	− 0·02
262	1·14	1·10	+ 0·04	− 0·02
284	1·35	1·32	+ 0·03	− 0·02
306	1·58	1·54	+ 0·04	− 0·01
331	1·84	1·82	+ 0·02	+ 0·01
358	2·12	2·07	+ 0·05	+ 0·04
413	2·66	2·61	+ 0·05	+ 0·11
1169	5·45	5·49	− 0·04	+ 0·04

SILVER ($\beta\nu = 215$; earlier value employed = 221).

T.	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye).	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
35·0	1·58	1·50	+ 0·08	− 0·01
39·1	1·90	1·88	+ 0·02	− 0·02
42·9	2·26	2·14	+ 0·12	+ 0·04
45·5	2·47	2·42	+ 0·05	+ 0·03
51·4	2·81	2·85	− 0·04	− 0·01
53·8	2·90	3·02	− 0·12	− 0·08
77·0	4·07	4·19	− 0·12	− 0·04
100	4·86	4·83	+ 0·03	+ 0·09
200	5·78	5·80	− 0·02	+ 0·01
273	6·00	6·04	− 0·04	− 0·02
331	6·01	6·13	− 0·12	− 0·11
535	6·46	6·46	0·0	+ 0·01
589	6·64	6·57	+ 0·07	+ 0·07

Copper gave an equally satisfactory result. On the whole Debye's equation applies more exactly even than the equation of Nernst and Lindemann. Debye's equation has of course the further advantage that it possesses a theoretical basis, whilst that of Nernst and Lindemann is semi-empirical.

NOTE on the method of evaluating the summation term of the Debye formula in the form given by Nernst and Lindemann.

To evaluate—

$$\sum_{n=1}^{n=\infty} e^{-n\frac{\beta\nu}{T}}\left(\frac{1}{n\frac{\beta\nu}{T}}+\frac{3}{n^2\left(\frac{\beta\nu}{T}\right)^2}+\frac{6}{n^3\left(\frac{\beta\nu}{T}\right)^3}+\frac{6}{n^4\left(\frac{\beta\nu}{T}\right)^4}\right).$$

Set $\frac{\beta\nu}{T}$ equal to x. Also set $e^{-1}=a$. Then $e^{-nx}=a^{nx}=(a^x)^n=y^n$ if y be set equal to a^x.

The sum can therefore be written:

$$\sum_{n=1}^{n=\infty} a^{nx}\left(\frac{1}{nx}+\frac{3}{n^2x^2}+\frac{6}{n^3x^3}+\frac{6}{n^4x^4}\right)$$

or the same expression may be written:

$$\underbrace{\sum_{n=1}^{n=\infty} a^{nx}\cdot\frac{1}{nx}}_{\text{First term.}}+\underbrace{\sum_{n=1}^{n=\infty} a^{nx}\cdot\frac{3}{n^2x^2}}_{\text{Second term.}}+\underbrace{\sum_{n=1}^{n=\infty} a^{nx}\cdot\frac{6}{n^3x^3}}_{\text{Third term.}}+\underbrace{\sum_{n=1}^{n=\infty} a^{nx}\cdot\frac{6}{n^4x^4}}_{\text{Fourth term.}}$$

$$\text{First term}=\frac{1}{x}\left[\frac{y}{1}+\frac{y^2}{2}+\frac{y^3}{3}+\ldots \textit{ad inf.}\right].$$

$$\text{Second term}=\frac{3}{x^2}\left[\frac{y}{1^2}+\frac{y^2}{2^2}+\frac{y^3}{3^2}+\frac{y^4}{4^2}+\ldots \textit{ad inf.}\right].$$

$$\text{Third term}=\frac{6}{x^3}\left[\frac{y}{1^3}+\frac{y^2}{2^3}+\frac{y^3}{3^3}+\frac{y^4}{4^3}+\ldots \textit{ad inf.}\right].$$

$$\text{Fourth term}=\frac{6}{x^4}\left[\frac{y}{1^4}+\frac{y^2}{2^4}+\frac{y^3}{3^4}+\frac{y^4}{4^4}+\ldots \textit{ad inf.}\right].$$

Each of these series is convergent, so that only the first three or four expressions in each need be taken into account.

Characteristic Infra-red Frequencies Obtained from Debye's Formula.—By means of equation (2) of the preceding section it is possible to calculate the characteristic infra-red frequency $\nu_{max.}$ (which represents the upper limit of the spectrum of vibrations) from a determination of the characteristic temperature θ. This temperature can be obtained in turn from the elastic constants of the substance as has been shown by Debye. Making use of Debye's values of θ, H. S. Allen (*Proc. Roy. Soc.*, **A**, **94**, 100 (1917)) has calculated $\nu_{max.}$ for the elements given in the following table. It will be observed that the frequencies so obtained agree very well with those calculated by methods previously mentioned:—

Atomic Frequencies by Debye's Formula.

Element.	$\nu_{max.} \times 10^{-12}$.
Al	8·26
Fe	9·67
Ni	9·01
Cu	6·81
Pd	4·22
Ag	4·39
Cd	3·48
Sn	3·83
Pt	4·68
Au	3·44
Pb	1·49
Bi	2·30

Molecular Heats of Polyatomic Solids, e.g. Salts.

It has already been mentioned that the Nernst-Lindemann equation does not take account of the molecular heats of salts in general, although it appears to do so for KCl, NaCl, and KBr. The Debye equation is equally inapplicable. Nernst proceeds therefore in the following manner:—

In the case of a polyatomic molecule in a *solid* there are two types of vibration to be considered; first, the vibration of the molecule as a whole, and secondly, the vibration of the atoms inside each molecule. This view, it will be observed, is difficult to reconcile with the conclusion arrived at, as a result of Br gg's work on crystals by the X-ray method, according to which molecules lose their identity in the solid state. Nevertheless the method employed by Nernst in connection with molecular heats of salts, etc., is highly successful, and must be considered, although an open mind has to be kept regarding certain of the assumptions. According to Nernst the mode of vibration of the *molecules* is taken account of by Debye's formula, whilst that of the *atoms* is taken account of by Einstein's formula. It is reasonable to treat the motion of atoms inside a molecule as closely analogous to that of the atoms in a monatomic solid, to which case Einstein's formula was intended to apply in the first instance. Nernst's method amounts therefore to a combination of Einstein's and Debye's formulæ. The frequency ν_1, *i.e.* the upper frequency employed in the Debye portion of the expression, is obtained from the melting-point formula of Lindemann, whilst the frequency ν_2 employed in the Einstein portion of the expression is that given directly by the Reststrahlen method.[1] On adding the two portions together the resulting expression gives the whole molecular heat of the solid. If C_v denotes, as before, the mean atomic (or half molecular) heat of a diatomic solid such as KCl, then $2C_v$ denotes the whole molecular heat of the solid at constant volume, and according to Nernst—

[1] ν_2 is greater than ν_1; hence at low temperatures there are practically no resonators possessing the quantum $h\nu_2$. That is, at low temperatures the *atoms* possess scarcely any energy of vibration whilst the *molecules* as a whole do possess energy of vibration.

$$2C_v = F_1\left(\frac{\beta\nu_1}{T}\right) + F_2\left(\frac{\beta\nu_2}{T}\right)$$

where F_1 and F_2 are the Debye and Einstein functions or atomic heat expressions respectively.

In the case of KCl, $\beta\nu_1 = 166$ (obtained from the melting-point formula), and $\beta\nu_2 = 213{\cdot}5$ (obtained directly from the Reststrahlen observations). The following table, taken from Nernst's *Theory of the Solid State*, gives the values of the Einstein and Debye portions of the molecular heat in the case of KCl. The column headed "correction" contains the quantities which must be added to $2C_v$ in order to give $2C_p$, the molecular heat at constant pressure :—

KCl . $\beta\nu_2 = 213{\cdot}5$; $\beta\nu_1 = 166$.

T.	Einstein.	Debye.	Correction.	Sum ($2C_p$ Calc.).	$2C_p$ Obs.
22·8	0·046	1·04	—	1·086	1·16
26·9	0·13	1·48	—	1·61	1·52
30·1	0·25	1·87	—	2·12	1·96
33·7	0·43	2·25	—	2·68	2·50
48·3	1·43	3·52	—	4·95	5·70
57·6	2·13	4·06	0·02	6·21	6·12
70·0	2·89	4·57	0·04	7·50	7·58
86·0	3·66	4·97	0·06	8·79	8·72
735	5·55	5·81	0·32	11·68	11·78
416	5·83	5·91	0·68	12·42	12·72
550	5·87	5·93	0·90	12·70	13·18

NaCl . $\beta\nu_2 = 282$; $\beta\nu_1 = 229$ (215).

T.	Einstein.	Debye.	Correction.	Sum.	$2C_p$ Obs.
25	0·010	0·610	—	0·62	0·58
25·5	0·012	0·637	—	0·65	0·62
28·0	0·027	0·794	—	0·82	0·80
67·5	1·65	3·56	0·02	5·23	6·12
69·0	1·73	3·63	0·02	5·38	6·26
81·4	2·39	4·13	0·04	6·56	7·08
83·4	2·49	4·20	0·06	6·75	7·50
138	4·26	5·22	0·16	9·64	9·74
235	5·29	5·68	0·42	11·39	11·52

AgCl . $\beta\nu_2 = 179$; $\beta\nu_1 = 102$ (114).

T.	Einstein.	Debye.	Correction.	Sum.	$2C_p$ Obs.
23·6	0·17	2·78	—	2·95	2·98
26·4	0·31	3·18	—	3·49	3·44
32·8	0·76	3·89	0·04	4·69	4·79
45·6	1·90	4·69	0·07	6·78	7·25
87·0	4·24	5·58	0·18	10·00	9·74
116	4·92	5·75	0·28	10·95	10·34
207·5	5·59	5·90	0·52	12·01	11·81
330	5·81	5·93	1·3	13·04	13·01
405	5·85	5·94	1·8	13·59	13·60
430	5·86	5·94	1·9	13·70	13·72

The numbers in brackets denote the values of $\beta\nu_1$ actually obtained by the melting-point method. They are very close to the values of $\beta\nu_1$ which are arbitrarily chosen.

An examination of the data given shows that at very low temperatures the contribution made by the Debye portion is much greater than that made by the Einstein portion, as we would expect.

It will be recalled that the Nernst-Lindemann formula applies fairly well to the case of KCl and NaCl, the frequency employed being that obtained by the Reststrahlen method. "This agreement must be regarded as half accidental, and may be explained on algebraic grounds from the approximation—

$$2F_1\left(\frac{\beta\nu}{T}\right) = F_1\left(0{\cdot}75\,\frac{\beta\nu}{T}\right) + F_2\left(\frac{\beta\nu}{T}\right).$$

In the case of KCl and NaCl the fundamental [molecular] frequency [ν_1 in the above table] is in fact about 0·75 times the internal [atomic] frequency [ν_2 in the above case]."

An interesting case is that of mercurous chloride. Taking the molecular formula to be HgCl and calculating the molecular heat by the above method, discrepancies are observed which lie outside experimental error. Nernst concludes therefore that in solid calomel the molecule Hg_2Cl_2 (and possibly a still more complex molecule) exists, which is in agreement with conclusions arrived at concerning the molecular formula of calomel in the dissolved state. "The exact complexity cannot yet be decided since the melting point of the salt is not open to observation on account of decomposition."

A further interesting case is that of ice. In order to account for the molecular heat of ice by the above method it is necessary to regard the molecular weight as 36 approximately (*cf.* Nernst, *The Theory of the Solid State*). Graphite and sulphur likewise show evidence of considerable polymerisation.

Although the method of treatment which has just been outlined is very ingenious, it is obviously of a somewhat hypothetical character in

its present formulation. It is not improbable that considerable modifications may eventually be introduced. It represents, however, a partially successful attempt to solve the problem of the heat capacity of polyatomic substances.

We shall conclude this chapter by quoting some numerical data obtained by Eucken (*Ber. Deutsch. phys. Ges.*, **18**, 4 (1916)) in connection with the heats of fusion and vaporisation of certain condensed gases at low temperatures :—

Substance.	Molecular Heat of Fusion in Calories.
Argon	267·9
Nitrogen	168·7
Oxygen	105·5
Carbon monoxide	224·1

Nitrogen was found to exist in two solid forms, the temperature of transition being 35·5° abs. and the molecular heat of transformation 53·8 cals. Oxygen exhibits three solid forms ; transition temperatures, 23·5° and 42·5° abs., the corresponding molecular heats of transformation being 17·5 and 167·4 cals. respectively. Carbon monoxide exists in two solid forms ; transition temperature, 60·4° abs., molecular heat of transformation, 144·1 cals.

Substance.	Molecular Heat of Vaporisation in Calories.
Hydrogen	229
Nitrogen	1363
Oxygen	1599
Argon	1501
Carbon monoxide	1414

Eucken (*loc. cit.*) has likewise measured the specific heats of solid and liquid argon, nitrogen, oxygen, and carbon monoxide ; the specific heats of solid carbon dioxide and of liquid hydrogen, and likewise the specific heat of highly compressed gaseous helium.

CHAPTER IV.

(Physical equilibrium in gaseous systems)—Molecular heats of gases—Bjerrum's theory—Krüger's theory.

BJERRUM'S THEORY.

In Chapter I. we have already had occasion to discuss briefly the problem of the molecular heats of gases. It has been pointed out that the observed values cannot be accounted for on the basis of the equipartition principle, especially the fact that the molecular heat varies with the temperature. In view of the considerable advance which has been made possible in the analogous case of solids by the application of the quantum theory, it is of interest to see how far the same considerations can be applied in the present case. This problem was first taken up by Bjerrum (*Zeitsch. Elektrochem.*, **17**, 731 (1911); *ibid.*, **18**, 101 (1912)).

In Chapter I. we have given a table showing the number of possible degrees of freedom, as estimated by Bjerrum, which are possessed by mono-, di-, tri-, and tetra-atomic gas molecules in respect of translation, rotation, and vibration. In the case of monatomic gases, which appear to possess translational energy only, the equipartition principle of classical statistical mechanics gives a satisfactory explanation of the observed values, *e.g.* the case of argon already discussed. So long as we restrict ourselves to translational movement the equipartition principle necessarily holds good, whether the molecule be monatomic or polyatomic; the distribution of energy in terms of the quantum theory only enters when we deal with vibrations or rotations, *i.e.* movement with respect to a centre of gravity.

As already pointed out, the result obtained in the case of argon leads us to regard a *mon*atomic gas as possessing no energy other than that of translation. This is somewhat unexpected, and we shall return to it later in connection with Kruger's theory. For the present, however, we are discussing Bjerrum's treatment.

As regards rotation of the molecule as a whole Bjerrum shows that the potential energy of rotation is negligible compared with the kinetic energy. (The case is quite different of course for the *vibrations* of the atoms inside the molecules.) In regard to vibration of one atom with respect to the other in a diatomic gas molecule, according to the quantum hypothesis the sum of the kinetic and potential energies, instead of being RT, is a fraction ϕ of this quantity. That is the total vibrational energy is ϕRT. ϕ is a function of the temperature T and

of the vibration frequency ν. According to Nernst and Lindemann we have—

$$\phi = \tfrac{1}{2}\frac{\beta\nu/T}{e^{\beta\nu/T} - 1} + \tfrac{1}{2}\frac{\beta\nu/2T}{e^{\beta\nu/2T} - 1}.$$

Bjerrum has investigated the Einstein function as well. It is found to hold fairly well, but is not so exact as that of Nernst and Lindemann. At absolute zero ϕ is zero, and at high temperatures ϕ approximates to unity, *i.e.* at high temperatures the conclusions based on classical statistical mechanics ought to hold good.

In the case of a triatomic molecule, containing the atoms A, B, and C, these may vibrate with respect to one another in pairs, *viz.* A with respect to B, B with respect to C, and C with respect to A. There are therefore three different vibrations to be taken account of, and the total vibrational energy is—

$$RT(\phi_1 + \phi_2 + \phi_3).$$

The following tables contain the data obtained in the case of a number of gases. The wave-length λ is that chosen by Bjerrum for substitution in the Nernst-Lindemann equation. The temperature T is in degrees absolute. $C_v(x°, T°,)$ denotes the *mean molecular* heat (at constant volume) over the temperature range between $x°$ abs. and T° abs.

Molecular Heat of Hydrogen.

The formula employed by Bjerrum is:—

$$C_v(0°, T°) = (5/2) \cdot R + R\phi[2{\cdot}0\mu]$$

where 5/2R covers the translational and rotational energy[1] of the mole-

[1] Bjerrum, as already pointed out, ascribes two degrees of freedom to a diatomic molecule, such as H_2, in respect of rotation of the molecule as a whole. By writing the corresponding energy term as RT (which then added to the 3/2RT, due to translation, makes in all 5/2RT), Bjerrum is here assuming that rotational energy may be treated from the standpoint of the equipartition principle. To get the contribution which translation and rotation make to the total molecular *heat* it is of course necessary to differentiate with respect to T, *i.e.* we obtain the term 5/2R. The same assumption of equipartition is employed in the other gases, the molecular heats of which are considered. In a later paper, however (*Nernst Festschrift*, 1912, p. 90), Bjerrum regards rotational energy of the molecule as a quantity which has to be treated from the quantum standpoint, the characteristic wave-length of molecular rotation lying far in the infra-red region (about 30μ in the case of hydrogen), whilst the characteristic wave-length of atomic *vibration* (inside the molecule) lies in the short infra-red region, between 1 and 10μ approx. In other words, molecular rotations are much less violent than atomic vibrations and require a much smaller quantum, *i.e.* a much smaller ν or greater λ. It has been observed that the atomic vibrations, instead of manifesting themselves as sharp lines in the short infra-red portion of the spectrum, actually exhibit bands more or less broad. An explanation of this has been suggested by Bjerrum on the following lines. The broadening is regarded as due to the presence of a number of "secondary" lines situated on either side of the principal atomic-vibration line, the latter being identified with the "head" of the band. These secondary lines are regarded as multiples or overtones of the fundamental rotational frequency or wave-length which occurs in the longer wave region. As the frequency of rotation is small its consecutive multiples will lie close together

cule and $2{\cdot}0\mu = \lambda$ is the characteristic wave-length of atomic vibration, which is of course connected with the frequency of atomic vibration by means of the relation $c = \lambda\nu$, where c is the velocity of light. The following table indicates the degree of agreement between the observed and calculated molecular heats of hydrogen :—

T Abs.	C_v (291°, T°,) Calculated.	C_v (291°, T°,) Observed.
1734	5·39	5·23
2083	5·51	5·44
2431	5·62	5·68
2647	5·69	5·76

Molecular Heat of Nitrogen. (Oxygen and carbon monoxide have the same molecular heat as nitrogen.)

Formula employed: $C_v(o°, T°,) = (5/2) . R + R\phi[2{\cdot}4\mu]$.

T Abs.	C_v (273°, T°,) Calculated.	C_v (273°, T°,) Observed.
473	4·97	4·73
903	5·12	4·91
1273	5·32	5·25
1620	5·47	5·31
	C_v (291°, T°,) Calculated	C_v (291°, T°,) Observed
1792	5·55	5·43
2057	5·65	5·58
2225	5·71	5·79
2446	5·78	5·87
2640	5·84	5·93

In the case of hydrogen the characteristic wave-length assumed for the atomic vibration is $\lambda = 2{\cdot}0\mu$; in the case of nitrogen, $\lambda = 2{\cdot}4\mu$. One would expect that if the vibrating particles are electrically charged that an absorption band should occur at these positions in the case of hydrogen and nitrogen. No bands, however, have been observed in this region of the spectrum. On the other hand, oxygen and carbon monoxide have the same molecular heat as nitrogen, and direct measurement has shown that oxygen possesses bands at $3{\cdot}2\mu$ and $4{\cdot}7\mu$, whilst carbon monoxide exhibits bands at $2{\cdot}4\mu$ and $4{\cdot}6\mu$. The bands

when they occur at all, and, in fact, by measuring the distance apart of the "secondary" lines referred to, it is quite possible to calculate the actual fundamental frequency of the rotation itself. On the basis of a calculation made by Rayleigh it can be shown that under certain conditions, if ν_1 is the vibration frequency of the atomic vibrations, and ν_2 is the much smaller frequency of the molecular rotations, then in the region of the spectrum in which the atomic vibration manifests itself we may expect in general three absorption lines occurring at the positions defined by $\nu_1 + \nu_2$, ν_1, and $\nu_1 - \nu_2$.

of oxygen are weak, and it is possible that hydrogen would exhibit a band if its absorption were measured when the gas itself were excited, *i.e.* at a fairly high temperature.

Molecular Heat of CO_2. (SO_2 has the same molecular heat.)

As this is a triatomic molecule we have three atomic vibrations to take account of. Two of these, however, may be expected to be the same, as the oxygen atoms are presumably linked symmetrically to the carbon atom. The translational energy plus the rotational energy are in this case, according to Bjerrum, represented by the term 3RT, *i.e.* 3/2RT translational and 3/2RT rotational. The wave-length of vibration of each of the oxygen atoms with respect to the carbon is taken by Bjerrum to be $5{\cdot}0\mu$; the wave-length of vibration of the two oxygen atoms against each other is taken to be $8{\cdot}1\mu$. The formula employed by Bjerrum is—

$$C_v(0°, T°,) = 3R + 2R\phi[5{\cdot}0\mu] + R\phi[8{\cdot}1\mu].$$

[Note that the second term on the right-hand side of this expression contains the number 2, to allow for the fact that there are two similar kinds of atomic vibrations present. It may also be pointed out that if CO_2 were a linear molecule, O = C = O, the rotational energy term would be RT (as in a diatomic gas). The fact that the value 3/2RT for the rotational energy agrees with experiment (*cf.* the following table) means that CO_2 is not a linear molecule, its spatial constitution being represented approximately by . The constitution of the CO_2 molecule is considered in detail by Bjerrum (*Verh. d. D. phys. Ges.*, **16**, 737, 1914).]

T Abs.	C_v (273°, T°,) Calculated.	C_v (273°, T°,) Observed.	C_v (273°, T°,) Calculated Employing the Wave-Lengths 2·7, 4·3, and 14·7μ.
473	7·44	7·48	7·67
903	8·67	8·60	8·47
1273	9·35	9·33	9·00
1637	9·80	9·84	9·40
1884	10·03	9·98	9·62
2112	10·21	10·28	9·81
2383	10·43	10·47	10·04

The agreement between observed and calculated values is satisfactory. We have now to see what evidence is available from the absorption spectrum of CO_2 as regards the choice of the wave-lengths employed. Direct measurement has shown that CO_2 possesses bands at $14{\cdot}7$, $4{\cdot}3$, and $2{\cdot}7\mu$. These are of the same order of magnitude as those used in the above formula. As a matter of fact, Bjerrum has also used the three observed values of λ and has obtained values for C_v which agree moderately with the observed. The formula in this case is—

$$C\ (0°, T°,) = 3R + R\phi[2{\cdot}7\mu] + R\phi[4{\cdot}3\mu] + R\phi[14{\cdot}7\mu].$$

The resulting values are given in the last column of the preceding table.

Molecular Heat of Water Vapour.

The formula employed by Bjerrum is—

$$C_v(o°, T°,) = 3R + 2R\phi[1{\cdot}3\mu] + R\phi[3{\cdot}6\mu] + \left(\frac{T}{3100}\right)^4.$$

The following values are thereby obtained:—

T Abs.	C_v Calculated.	C_v Observed.	Remarks.
323	6·02	5·96	These values are true molecular heats, *i.e.* instantaneous values for the temperatures referred to, not mean values over a wide range of temperature.
543	6·34	6·40	
723	6·67	6·80	
	C_v (383°, T°,) Calculated	C_v (383°, T°,) Observed	
893	6·55	6·51	Mean values for the molecular heat over the temperature range indicated.
1273	6·95	6·95	
1600	7·36	7·40	
	C_v (291°, T°,) Calculated	C_v (291°, T°,) Observed	
2084	7·99	7·92	
2383	8·54	8·54	
2650	9·14	9·37	Ditto.
2936	9·9	10·0	
3181	10·7	10·5	
3337	11·3	10·9	

The absorption spectrum of water vapour contains many bands over the range of λ's employed above, *i.e.* bands at 1·1, 1·5, 2·0, 3·2, 4·7μ, etc. Where there are so many bands almost any value might be regarded as borne out by the absorption spectrum. It appears from this and other cases that the calculated molecular heat is not very sensitive to error in the actual value chosen for λ. The term $\left(\frac{T}{3100}\right)^4$ is a purely empirical term introduced by Bjerrum to account for the fact that the molecular heat of water vapour increases with the temperature more rapidly than would be anticipated on the basis of the quantum theory. The cause of this is by no means clear: possibly it is connected with a depolymerisation of any bimolecules which may be present, though at the higher temperatures this would be a negligible quantity.

The molecular heat of ammonia, a tetra-atomic body, may likewise be calculated more or less satisfactorily by writing down terms for

translation and rotation, and by applying the quantum theory to the vibrations of the atoms, using the wave-lengths $2{\cdot}1\mu$ and $8{\cdot}9\mu$ which actually occur in the absorption spectrum of ammonia.

It is evident from the foregoing that to account for the observed values of the molecular heats of gases it is essential to introduce the quantum theory in some form. Bjerrum's mode of treatment, though marking a considerable advance, is open to criticism, more particularly as regards the choice of the number of degrees of freedom.

We shall consider later the views put forward by Krüger in connection with the same problem.

One point remains to be emphasised in connection with the molecular heat, or rather the energy content of gases. Owing to the fact that the true atomic vibrations inside the molecule correspond to relatively high frequencies (*i.e.* short infra-red region) such vibrations contribute a relatively small amount to the total energy content; for as the frequency is high very few molecules will possess even one quantum of this type of energy. The so-called rotational frequencies (obtained on applying the quantum theory to rotation) are much more important as they occur in the longer infra-red region.

The Absorption Spectrum of Water Vapour and of Hydrogen Chloride Gas in the infra-red region, from the point of view of Molecular Rotations, treated on the basis of the Quantum Theory.

As already mentioned, Bjerrum has treated the rotational energy of the di- or tri-atomic gas molecule from the point of view of the quantum theory. That is, the rotational spectrum should exhibit a number of lines related to one another by a constant frequency difference; this, at any rate, is the simplest possible statement. The spectrum due to such rotations would be expected to lie in the farther infra-red (beyond 10μ), the principle lines in the shorter infra-red region being due to the *vibrations* of the *atoms* inside the molecule. Bjerrum assumes that the *total* rotational energy varies in terms of quanta, and as a further simplification he assumes that the moment of inertia of the molecule for all axes through the centre of gravity is the same; *i.e.* we have only to deal with one such moment. The energy of rotation of a particle round an axis is given by the expression $1/2 \cdot I \cdot (2\pi\nu)^2$, where ν is the frequency of rotation and I is the moment of inertia. On the older quantum theory this energy must be represented by $h\nu$, $2h\nu$, etc., or in general by $nh\nu$, where n is a whole number. Hence we have—

$$1/2\ I \cdot (2\pi\nu)^2 = n \cdot h\nu$$

or,

$$\nu = n \cdot h/2\pi^2 \cdot I.$$

According to this expression we would expect a difference series in the frequencies of the band heads in the spectrum of a gas. That is, harmonics of the fundamental rotational frequency are to be expected in the spectrum according to the value ascribed to n. From an examination of the spectrum of water vapour Bjerrum concludes that the frequency difference in the series of rotational bands is $1{\cdot}73 \times 10^{12}$. He

then proceeds to consider the spectrum between the limits 10μ and 20μ, ascribing all the band heads therein to rotations, n being given consecutive values from 10 to 16. The corresponding wave-length series (in μ) is given by the expression—

$$\lambda = \frac{3 \times 10^{14}}{\nu} = \frac{3 \times 10^{14}}{n \times 1{\cdot}73 \times 10^{12}}.$$

The following table indicates the degree of concordance obtained by this means :—

n.	=	16.	15.	14.	13.	12.	11.	10.
λ	Calculated.	10·8	11·6	12·4	13·3	14·4	15·8	17·3μ
λ	Observed.	10·9	11·6	12·4	13·4	14·3	15·7	17·5μ

With increasing wave-length the bands become deeper and tend to overlap. For wave-lengths greater than $17{\cdot}5\mu$ the absorption becomes general and without structure unless very good dispersion is obtained in the apparatus. Whilst these results are to be regarded as a considerable step in our understanding of the problem of the source of bands, the numerical results just quoted are, according to E. von Bahr, open to a certain amount of doubt (*Verh. d. D. phys. Ges.*, **15**, 731 (1913)).

At sufficiently high temperatures the energy of rotation will be directly proportional to the absolute temperature. Hence, the frequency of rotation will be directly proportional to the square root of the temperature, since the rotational energy term involves ν^2. Hence, the product of the rotational wave-length into $\sqrt{T}$ should be a constant. The rotational wave-length is obtained in the following way. In the *short* infra-red region (*i.e.* the region of the spectrum in which the bands are due to ordinary vibrations of atoms inside the molecule) it is to be expected, on the basis of Rayleigh's considerations, already referred to, that, instead of a single well-defined band head due to vibration, we should find a triple-headed band, *viz.* a centre one due to atomic vibration and two others due to compounded rotational and vibrational motion. As a matter of fact, what is frequently found with a certain degree of dispersional power in the spectrometer, is a double-headed band. E. von Bahr suggests that the middle band is not really missing, but only apparently so, on account of insufficient dispersion. The two wave-lengths λ_1 and λ_2, which in general lie fairly close together, correspond to two frequencies ν_1 and ν_2, and their difference $(\nu_2 - \nu_1)$ is just twice the most probable frequency ν_r of the rotation. ν_r is of course considerably smaller than either ν_1 or ν_2 and its normal position is far in the infra-red. On expressing ν_r in terms of its wave-length λ_r we find that $\lambda_r = 2\frac{\lambda_1 . \lambda_2}{\lambda_1 - \lambda_2}$. The above is a convenient way of measuring the rotational wave-length without having to investigate the far infra-red

region. The validity of the expression can of course be tested by comparison with actual measurements in the far infra-red where the bands are due to rotation only. From what has been said above, it follows that the product $\frac{\lambda_1 . \lambda_2}{\lambda_1 - \lambda_2} . \sqrt{T}$ should be a constant, provided the theoretical considerations are sound. Making use of some data obtained by Paschen in the region 5 to 6μ in the case of water vapour, E. von Bahr has found that the two heads of the double band (due to molecular rotations compounded with atomic vibration) alter their relative position in accordance with the above expression.

°C.	λ_1.	λ_2.	$\sqrt{T} . \frac{\lambda_1 . \lambda_2}{\lambda_1 - \lambda_2} \times 10$.
17	6·512	5·948	1·17
100	6·527	5·900	1·19
600	6·563	5·607	1·14
1000	6·597	5·416	1·08
1470	6·620	5·377	1·20

In view of the fact that the temperature measurements were not very exact, the constancy of the expression in the last column is very satisfactory.

E. von Bahr has investigated more closely the constitution of the bands of water vapour between 5 and 6μ and has found that each exhibits a number of sub-maxima. Similar behaviour is shown by other gases. That is, the *discontinuous* nature of the absorption required by the quantum theory is fully borne out. From measurements of the positions of the successive sub-maxima it is found in the case of water vapour that the largest value for λ_r is of the order 400μ, *i.e.* water vapour should exhibit absorption at various positions down to this region, a result in agreement with the observations of Rubens. On the other hand, the experimental results obtained by E. von Bahr indicate a lack of symmetry with respect to the principal maximum of a given band, which indicates in turn that a *single* frequency difference is insufficient to account for the whole series of band heads.

The question of the rotational spectrum of water vapour, *i.e.* the infra-red spectrum beyond 10μ, has also been investigated by Eucken (*Verh. d. D. phys. Ges.*, **15**, 1159 (1913)), who adopts Bjerrum's expression for the series of frequencies to be expected, *viz.*

$$\nu = n . h/2\pi^2 . I.$$

This expression is based upon the assumption that the molecule is symmetrical, and possesses therefore but one moment of inertia. Eucken, however, emphasises the lack of symmetry of the water molecule and ascribes to it at least two principal moments of inertia, which would lead us to expect two different series in the spectrum. Sackur (*Ann. physik*, [iv.], **40**, 95 (1913)) has arrived at the conclusion—on quite other

grounds—that the water molecule possesses two main moments of inertia, which are in the ratio of 1 : 2. Eucken finds, on taking two values for I, one of which is approximately twice the other, and calculating the corresponding series as given by the Bjerrum expression, that satisfactory agreement is obtained between the calculated and observed band maxima. The following table contains Eucken's results :—

INFRA-RED ABSORPTION BANDS OF WATER VAPOUR.

λ Observed (in μ).		λ Calculated (in μ).			
Direct.[1]	Indirect.[2]	First Series. $I = 0{\cdot}96 \times 10^{-40}$.	*n*.	Second Series. $I = 2{\cdot}21 \times 10^{-40}$.	*n*.
10·9μ	—	10·8μ	16	—	—
11·6	—	11·6	15	—	—
12·4	—	12·4	14	—	—
13·4	—	13·3	13	—	—
14·3	—	14·4	12	—	—
15·7	—	15·8	11	—	—
17·5	—	17·3	10	—	—
—	—	19·3	9	—	—
—	—	21·6	8	—	—
—	25μ	24·8	7	25·0μ	16
—	27	—	—	26·7	15
—	28	28·9	6	28·5	14
—	30	—	—	30·7	13
—	33	34·7	5	33·3	12
—	36	—	—	36·5	11
—	39	—	—	40·0	10
—	42	43·3	4	—	—
—	45	—	—	44·5	9
50	47-50	—	—	50·0	8
ca. 58	54-56	57·8	3	57·2	7
66-67	64-69	—	—	66·6	6
78-80	79-81	—	—	80·0	5
—	91 92	87	2	—	—
ca. 103	109	—	—	100	4
—	124-128	—	—	133	3
—	170-172	173	1	—	—
—	240-250	—	—	200	2
—	385-398	—	—	400	1

E. von Bahr (*ibid.*, **15**, 1154) has examined very carefully a simpler case than that of water vapour, namely, the infra-red spectrum of HCl gas. The subdivision of each part of the double band (found by Burmeister and shown by the dotted line in the figure) into twelve separate maxima is very clearly shown in Fig. 9.

The data corresponding to Fig. 9 are given in the following table. The wave-lengths λ_1 and λ_2 of the right and left parts of the double absorption band, as well as the corresponding frequencies, are given.

[1] Rubens and Aschkinass, *Wied. Ann.*, **64**, 584, 1898; Rubens, *Ber. Berliner Akad.*, 1913, p. 513.

[2] E. von. Bahr, *Verh. D. phys. Ges.*, **15**, 731, 1913.

The first column contains the value of n, *i.e.* the order of that maximum reckoned from the middle of the absorption band. The middle of the

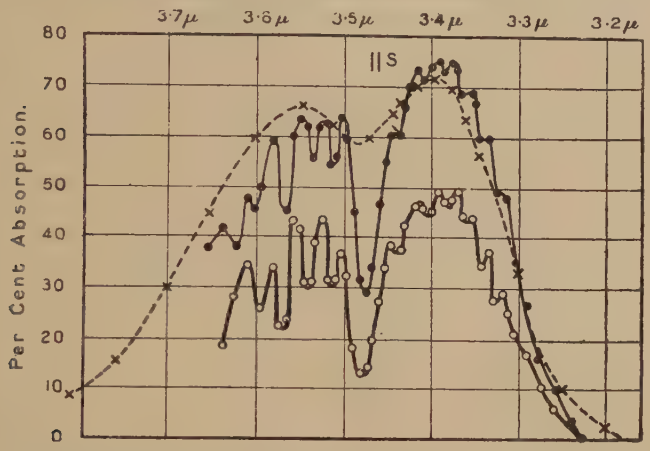

FIG. 9.—*Hydrogen chloride gas* (E. von Bahr). S denotes slit width. Dotted curve due to Burmeister. Upper full curve corresponds to 760 mm.; lower full curve corresponds to 380 mm.

absorption band is characterised by the wave-length $\lambda_0 = 3{\cdot}474\mu$, and the frequency $\nu_0 = 8{\cdot}636 \times 10^{13}$.

HYDROGEN CHLORIDE GAS.

n.	λ_1 in μ.	λ_2 in μ.	$\nu_1 \times 10^{-13}$.	$\nu_2 \times 10^{-13}$.
1	3·444	3·504	8·711	8·562
2	3·416	3·528	8·782	8·503
3	3·394	3·556	8·839	8·436
4	3·372	3·583	8·897	8·373
5	3·352	3·610	8·950	8·310
6	3·332	—	9·004	—
7	3·317	—	9·044	—

In the following table are given the values of $(\nu_1 - \nu_0)$ and $(\nu_0 - \nu_2)$, which, according to Bjerrum, should be equal to the rotational frequencies of the molecule of HCl:—

n.	$\nu_1 - \nu_0 \times 10^{-11}$.	$\nu_0 - \nu_2 \times 10^{-11}$.	$\nu_\gamma \times 10^{-11}$ mean.	λ_γ in μ.	$\frac{\nu_\gamma}{n} \cdot 10^{-11}$.
1	7·5	7·4	7·45	403	7·45
2	14·6	13·3	13·95	215	6·98
3	20·3	20·0	20·15	149	6·72
4	26·1	26·3	26·20	115	6·55
5	31·4	32·6	32·0	94	6·40
6	36·8	—	36·8	82	6·13
7	40·8	—	40·8	74	5·83

On Bjerrum's theory we would expect ν_r/n to be constant. As a matter of fact it is moderately constant over a considerable range but shows a definite tendency to diminish as n increases. E. von Bahr regards the variation as outside the limit of experimental error, although Eucken (*loc. cit.*) considers the question as not yet definitely settled. By employing the Bjerrum theory it is seen that HCl should absorb at several positions down to $\lambda = 400\mu$. Rubens and von Wartenberg (*Verh. d. D. phys. Ges.*, **13**, 796 (1911)) have found considerable absorption exhibited by this substance in the residual-ray range, the absorption being especially strong at 150μ.

Bjerrum (*Verh. d. D. phys. Ges.*, **16**, 640 (1914)) recalculates the rotation frequencies of HCl in a manner somewhat different from that employed by E. von Bahr, and concludes that the agreement is as good as can be expected in view of the unavoidable experimental error in determining the position of the successive sub-maxima.

Whilst we are dealing with inter-relations between different portions of the infra-red spectrum, it is convenient to refer briefly to certain applications of Bjerrum's theory of molecular rotations which have been made by Baly (*Phil. Mag.*, **27**, 632 (1914); *ibid.*, **29**, 223 (1915); *ibid.*, **30**, 510 (1915)) in connection with the structure of bands exhibited by substances in the ultra-violet region. According to Baly the frequency of the central position of such a band must be a multiple of the principal frequency exhibited in the infra-red region by the same substance. Further, the breadth which such ultra-violet bands possess is due to a number of lines lying close together, and the distances apart of these lines, when expressed in terms of frequencies, are found to have constant values, and are to be ascribed, according to Baly, to the existence of certain basis constants characteristic of the molecule, these basis constants being also capable of accounting for the infra-red absorption of the molecule. This method of linking up the infra-red and ultra-violet absorption spectra has found considerable support in the spectra of benzene and other organic compounds, and particularly so in connection with the absorption of gaseous sulphur dioxide which has been examined by Garrett (*Phil. Mag.*, **31**, 505 (1916)) and by Miss Lowater (*Astrophys. Journ.*, **31**, 311 (1910)). Thus Garrett has found that the optical centre of the marked absorption band of SO_2 in the near ultra-violet occurs at $\lambda = 296{\cdot}1\mu\mu$, the corresponding wave-number (*i.e.* reciprocal of wave-length) being 3378. On applying the quantum hypothesis as Baly has done in this case we would expect that this wave-number should be an even multiple of the principal infra-red band of SO_2. The infra-red spectrum of SO_2 has been examined by Coblentz (*Pub. Carnegie Inst., Washington*, 1905) and has found a pronounced band at $7{\cdot}4\mu$ or wave-number $135{\cdot}1$. If this wave-number be multiplied by 25 we obtain the number $3377{\cdot}5$, which is almost identical with the centre of the ultra-violet band as determined by Garrett. For details of the method of determining the basis constants the papers referred to must be consulted. At the present time the mechanical significance of these constants is not clear. The accuracy, however, with which they

permit of even very complex spectra being calculated in detail indicates quite clearly that there is a very close connection between the infra-red and the ultra-violet absorption of any substance. This question is taken up briefly at a later stage (in Chap. VI.) in connection with the selective photo-electric effect.

Krüger's Theory.

(*Cf.* Krüger, *Ann. Physik*, [iv.], **50**, 346; *ibid.*, **51**, 450 (1916).)

Krüger assumes on the basis of the now generally accepted Rutherford-Bohr structure of atoms and molecules (*cf.* Chap. V.) that gaseous molecules must be gyroscopic in nature; that is, such molecules are quite incapable of *rotations*, but are capable of carrying out *precessional vibrations* (*cf.* Chap. I.). These vibrations are totally distinct from the ordinary vibration of two atoms along the line joining their centres, to which we have already referred in dealing with Bjerrum's treatment. As a result of collisions with other molecules Krüger considers that the ring of rotating electrons in a molecule, which serves to unite the two atoms together (in the case of a diatomic molecule), suffers displacements perpendicular to its direction of motion, with the result that the atoms themselves describe small circular orbits and the molecule as a whole exhibits motion of the precessional type. Such precession has already been shown diagrammatically in Chapter I. Krüger points out that such precessional motion is entirely kinetic and necessarily involves two degrees of freedom. In the temperature range in which the principle of equipartition holds good the energy term corresponding to these two degrees of freedom will be RT, which is identical in magnitude with that postulated by Bjerrum for a diatomic molecule on the basis of rotation of the molecule as a whole over the same temperature region. Over this range therefore the numerical values for the energy term is the same on either view in the case of a diatomic molecule.

The chief advantage of Krüger's theory lies however in the explanation which it offers of the behaviour of monatomic gases. Monatomic molecules, such as that of argon, possess energy which is completely taken account of by the free translation alone. An atom is therefore incapable of rotation. If molecular rotations were possible in general we would expect monatomic molecular rotations to be possible also. The theory of molecular rotations is not very satisfactory in this connection. On the other hand, Krüger shows that precessional vibrations in the case of a spherical monatomic molecule become practically infinitely rapid, and may therefore be left out of account in regard to the energy content. This conclusion becomes clearer when we introduce the quantum hypothesis.

At low temperatures it is necessary to treat all kinds of constrained motion, such as ordinary atomic vibrations, precessional vibrations or rotations from the standpoint of the quantum theory. The molecular heat in virtue of any of these types of motion decreases with falling

temperature and converges to zero at absolute zero of temperature. In the special case of a monatomic molecule in which the precessional vibrations are exceedingly rapid the corresponding quantum must be exceedingly great, and consequently the likelihood of any molecule possessing even one such quantum is negligibly small. In other words, the observed energy content can only be due to the free translational motion which is always directly proportional to the absolute temperature, *i.e.* the molecular heat in such a case is 3/2R, in complete agreement with experiment. In the case of diatomic gases Krüger has shown that the vibration frequencies of precession correspond to the farther infra-red region, about 30μ in the case of hydrogen, and that the so-called rotation spectrum is really due to precessional vibrations. It is only at high temperatures that the precessional vibration becomes so violent as to merge into a rotation (*cf.* Chap. I.). It must be clearly understood that the conflicting views of Bjerrum and Krüger have nothing to do with the ordinary atomic to-and-fro vibration inside the molecule, which Bjerrum has shown gives rise to bands in the short infra-red region, *i.e.* at wave-lengths shorter than 10μ.

On the whole, Krüger's view serves to bring the behaviour of monatomic and diatomic gases into much closer accord than had hitherto been the case. Considerable experimental work is still necessary, however, before we can decide between the theory of molecular rotations and the theory of precessional vibrations.

A translation of the major part of Krüger's papers will be found in Appendix III. for those desirous of following Krüger's treatment in greater detail.

The Molecular Heat of Hydrogen Gas at Low Temperatures.

(*Cf.* A. Eucken, *Sitzungsber. kön. preuss. Akad. Wissenschaft*, p. 141, 1912.)

The molecular heat of hydrogen is of particular interest because hydrogen is the simplest type of diatomic molecule. The most striking result obtained by Eucken is that at low temperatures hydrogen behaves as a monatomic gas, *i.e.* it exhibits no energy of a rotational or of a gyroscopic kind. The experimental details will be found in the paper referred to. It is sufficient in the present instance to quote certain of the results. Eucken employed different quantities of hydrogen in the calorimeter (internal volume, 39 c.cs.), and his experiments are sufficiently exact to show that the molecular heat varied with the concentration of the gas. The following table gives the value of the molecular heat observed corresponding to a particular temperature,[1] and the mass of hydrogen employed :—

[1] The molecular heat values are "instantaneous," or true molecular heats *at* a given temperature; not mean values over a temperature range.

T Abs.	Gram-moles of H_2.	Molecular Heat.
273·1	0·0966	4·94
194	0·1710	4·39
91	0·3550	3·44
91	0·1315	3·32
82	0·1268	3·30

The data obtained at still lower temperatures are given in the following table :—

T Abs.	Gram-moles H_2.	Molecular Heat.	Gram-moles H_2.	Molecular Heat.	Gram-moles H_2.	Molecular Heat.
35	0·1909	3·42	0·1794	—	0·1040	3·20
40	,,	3·28	,,	—	,,	3·18
45	,,	3·30	,,	3·28	,,	3·13
50	,,	—	,,	—	,,	3·13
60	,,	—	,,	—	,,	3·09
65	,,	3·21	,,	—	,,	3·14
70	,,	3·26	,,	—	,,	3·16
80	0·2585	3·29	0·1295	3·23	,,	3·20
85	,,	3·34	,,	3·27	,,	3·32
90	,,	3·42	,,	3·31	,,	—
100	,,	3·64	,,	3·37	,,	—
110	,,	3·82	,,	3·62	,,	—

It will be seen that the lower the concentration of the gas the lower the molecular heat.[1] This effect is taken account of by the thermodynamic relation—

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

To make use of this expression Eucken employs a relation of D. Berthelot which connects the molecular heat at any given concentration with that of the substance in the ideal gas state.[2] In this way Eucken arrives at the following values for the molecular heat of hydrogen in the ideal gas state :—

[1] This is not true universally for hydrogen, *i.e.* at very high pressures there is a tendency for C_v to diminish.

[2] Berthelot's expression involves the critical temperature and critical pressure of the gas.

MOLECULAR HEAT OF HYDROGEN IN THE IDEAL GAS STATE.

T Abs.	Molecular Heat.
35	2·98
40	2·98
45	3·00
50	3·01
60	2·99
65	3·04
70	3·10
80	3·14
85	3·21
90	3·26
100	3·42
110	3·62
196·5	4·39
273·1	4·84

These values show that the molecular heat of hydrogen falls rapidly with a fall in temperature, finally (at about 60° abs.) attaining a value 2·98, identical with that of a monatomic gas. Eucken finds that the molecular heat curve shows even a more rapid fall than that given by the Einstein formula for monatomic solids. The reason of the rapid fall is not clear; Eucken discusses the question in the paper referred to. The most striking fact, as already stated, is that at low temperatures the molecule of hydrogen possesses only energy of translation. Possibly other diatomic gases behave similarly; nothing is known on this point.

Eucken (*Ber. Deutsch. phys. Ges.*, **18**, 4 (1916)) has measured the molecular heats of hydrogen and helium at high pressures and at low temperatures, and has found that when the gases are strongly compressed, the molecular heat falls below the value 3/2R(2·98). This is discussed by Nernst (*Zeitsch. Elektrochem.*, **22**, 185 (1916)), who regards this "degradation of the ideal gaseous state" as due to the substitution of circular rotational motion of the molecules at very low temperatures in place of free translation. Thus, instead of the energy of the gas being expressed by the relation: $E = 3/2RT$ (due to translation), we have to substitute the expression—

$$E = \frac{3}{2}R \cdot \frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1}$$

where ν is the frequency of rotation. This expression can give rise to a molecular heat which is less than 3/2R. Experiment shows, however, that even at fairly low temperatures the relation $E = 3/2RT$ holds good, so that the second expression is only of importance at very low temperatures.

As a result of this modified expression for the energy of the gas which is functioning as a monatomic one, it follows that, under the same extreme conditions, in place of the perfect gas law $P = RT/V$ we must write—

$$P = \frac{R}{V} \cdot \frac{\beta_0 \nu}{1 - e^{-\beta_0 \nu / T}}.$$

The most striking conclusion arrived at by Nernst (*loc. cit.*; also *Verh. Deutsch. phys. Ges.*, p. 99 (1916)) is that this "degradation phenomenon" stands in close causal connection with the chemical constant of the gas, *i.e.* the quantity $\frac{i + \log R}{2{\cdot}3023}$ where i is the integration constant of the Clapeyron equation for the vapour pressure of the liquified substance. We have already discussed the significance of the chemical constant in connection with the application of Nernst's Heat Theorem to gaseous reactions.

Nernst finds theoretically that the chemical constant of a monatomic substance, or a substance which functions as such, can be expressed by a relation of the form—

$$C = C_0 + 1{\cdot}5 \log_{10} M,$$

where M is the gram-molecular weight of the substance, C is the chemical constant (identical with the C_0 of Chap. III., Vol. II.), and C_0 in the present instance is a constant independent of the nature of the substance considered. Nernst shows from an examination of the most reliable data existing at present that an expression of this form is in agreement with the experimental values of C. Nernst's theoretical expression is likewise in agreement with those of Sackur (*Nernst Festschrift*, p. 405; *Ann. Physik*, **40**, 67 (1913)), and of Tetrode (*Ann. Physik*, **38**, 434; **39**, 255 (1912); *Proc. Acad. Amsterdam* (1915)).

By introducing the quantum theory into a vapour pressure relation based upon his Heat Theorem, Nernst calculates C_0 to be $-1{\cdot}590$, the unit of pressure being the atmosphere, which is in good agreement with the mean observed value, namely, $-1{\cdot}62$ obtained from a consideration of the data available in connection with hydrogen, argon, monatomic iodine gas, and mercury vapour. Tetrode's (calculated) value for C_0 is $-1{\cdot}608$.

CHAPTER V.

(Physical equilibrium, *continued*)—Distribution of electrons in atoms—Structure of the atom from the standpoint of the quantum theory—The Rutherford-Bohr atom-model—Parson's magneton and the structure of the atom—High frequency spectra of the elements—Moseley's relation.

The Rutherford Atom-model.

(Rutherford, *Phil. Mag.*, [vi.], **21**, 669 (1911).)

THE underlying idea in this atom-model is that the atom consists of a central charge, concentrated on a nucleus, which is surrounded by an "atmosphere" of electrons, rotating in certain orbits. Practically the whole mass of the atom is to be ascribed to the nucleus. The number of "atmosphere" electrons is not large. The dimensions of the nucleus are considerably smaller than the dimensions of the atom as a whole. Rutherford estimates the diameter of the nucleus to be of the order 10^{-12} cm., whilst the diameter of the atom as a whole is of the order 10^{-8} cm. The nucleus itself possesses a structure about which, however, nothing is known. It, the nucleus, contains probably quite a large number of electrons, but these are bound firmly, except in the case of radioactive materials which are capable of expelling one of these bound electrons in the form of β-rays. The outermost ring of the "atmosphere" electrons contains those which give the property of valency to the atom. The innermost electron of the atmosphere is the source of X-rays, the shortest wave-length which the atom is capable of emitting. The necessary disturbance of the innermost electron is brought about by collision with a β-ray (cathode ray) which jerks the innermost electron out; on its return journey to the innermost ring it causes the emission of the extremely short waves which we call X-rays. Rutherford was led to this planetary view of the atom in order to explain the scattering of α and β particles. When such particles pass very close to the centre of an atom they are violently deflected, an effect which could be produced by a nucleus of the kind referred to. The angle of scattering has been measured by Geiger and Marsden in the case of α-rays, and by Crowther in the case of β-rays. The outer "atmosphere" of electrons rotating in rings do not appreciably affect the direction of the motion of an α particle travelling through the atom. It is only when the α particle comes into close contact with the nucleus that its path is abruptly altered, the path becoming hyperbolic.

Bohr's Application of the Quantum Theory to the Rutherford Atom-model.

(Bohr, *Phil. Mag.*, [vi.], **26**, i., 476, 857 (1913); *ibid.*, **27**, 506 (1914); **30**, 394 (1915).)

The following is a brief account of the line of thought pursued by Bohr, given to a large extent in his own words.

Bohr first of all points out that the Rutherford atom-model, which has just been referred to, suffers from the serious drawback that the system of "atmosphere" electrons is unstable; that is, unstable from the standpoint of classical electro-dynamics. If, however, we introduce Planck's concept, the instability may no longer exist from the theoretical point of view. The problem of atomic structure affords therefore a further instance of the necessity of introducing some new concept, such as that of Planck, into electro-dynamics in order to account for the observed facts. Bohr first attempts to apply the quantum theory to the process whereby a free electron—such for example as exists in a vacuum tube when a discharge is passed—may be conceived of as attaching itself to a positively charged nucleus. It will be shown that it is possible from the point of view taken to account, in a simple way, for the Balmer law of line spectra of hydrogen and helium, and possibly the theory will eventually be capable of dealing with the spectra of more complicated atomic structures.

According to Rutherford, the hydrogen atom consists of a nucleus with a single electron describing a closed orbit around it. The first assumption is that the mass of the electron is negligible compared with the mass of the nucleus, and that the velocity of the electron is small compared with that of light. Bohr considers that whilst the electron is rotating in this orbit or stationary state it is neither radiating or absorbing energy. Such rotation represents an equilibrium condition of the system as a whole. The production of spectra must be due therefore to some kind of departure from an equilibrium state. In general Bohr considers the possibility of a series of such stationary states corresponding to electron orbits of different radius, and *emission or absorption of radiation is due to the electron passing from one stationary or equilibrium state to another*. The quantum idea is introduced in the further hypothesis that during the passage of the electron from one equilibrium state to another, homogeneous radiation of a certain frequency ν is emitted or absorbed, the amount of radiant energy so emitted or absorbed being $h\nu$, where h is Planck's constant. It will be realised at once how very different these considerations are from those based on classical electrodynamics. On the classical view a charged particle rotating steadily in a closed orbit is giving off radiation continuously, and in so doing its orbit gradually becomes smaller so that the electron would finally drop into the nucleus. Furthermore, with the alteration in orbit the wave-length of the light emitted would gradually change, a conclusion which is opposed to direct observation, for spectra are clearly characteristic and unchangeable properties of an atom. Bohr assumes that no radiation at all is given out when the electron is rotating in an orbit.

Let us now consider the hydrogen atom—one in which there is a single nucleus carrying unit positive charge with one valency electron rotating round it—in a state of equilibrium, the electron traversing an elliptical orbit with a frequency of revolution ω, the major axis of the orbit being $2a$. The amount of energy W which must be given to the system (*i.e.* which the system must absorb) in order to remove the electron to an infinitely great distance (*i.e.* to dissociate the atom into a positively charged nucleus and a free electron), is connected with ω and $2a$ by the two following relations :—

$$\omega = \frac{\sqrt{2}}{\pi} \cdot \frac{W^{3/2}}{eE\sqrt{m}} \text{ and } 2a = \frac{eE}{W} \quad . \quad . \quad . \quad (1)$$

where e is the charge on an electron, E the charge on the nucleus, and m the mass of an electron. Further it can be shown that the kinetic energy of the electron taken for a complete revolution when it is rotating in one of it orbits is equal to W, the work required to eject the electron entirely from the system. Note that removal of the electron necessitates absorption of radiant energy.

Now let us consider the reverse process, namely, the act of binding a free electron to the nucleus. At the beginning the electron may be regarded as possessing no sensible velocity with respect to the nucleus, *i.e.* its frequency of revolution is zero relatively to the nucleus. The electron, after interaction has taken place, settles down to a stationary orbit—the word stationary refers to the orbit, the electron itself is in rapid rotation round the orbit. Bohr now takes the orbit as circular for reasons given later in connection with the physical significance of h. The initial free state of the electron represents the extreme limit of a series of stationary states through which the electron is capable of passing. The other limit is given by the smallest value of $2a$ or the greatest value of ω which necessitates the maximum value of W.

Let us assume that during the act of binding of the free electron to the nucleus, a homogeneous radiation of frequency ν is emitted. This frequency is, according to Bohr, just half the frequency of rotation ω of the electron in its final orbit. On the basis of Planck's theory we would expect that the total amount of radiant energy thus emitted would be $\tau h\nu$ where τ is a whole number. The assumption that the frequency ν is just $\omega/2$ suggests itself, since the frequency of revolution at the beginning of the binding process is zero and at the end of the process is ω, the mean or average of the two being $\omega/2$. Bohr gives a more rigorous treatment of this point in the first paper referred to. Since $\tau h\nu$ is the amount of energy emitted whilst the electron is approaching the nucleus from an infinite distance, and W is the amount of energy which has to be absorbed to make it reverse the operation, it follows that—

$$W = \tau h\nu = \tau h\frac{\omega}{2} \quad . \quad . \quad . \quad . \quad (2)$$

Combining thus with the equation (1) we obtain—

$$W = \frac{2\pi^2 me^2 E^2}{\tau^2 h^2}\ ;\ \omega = \frac{4\pi^2 me^2 E^2}{\tau^3 h^3}\ ;\ 2a = \frac{\tau^2 h^2}{2\pi^2 meE} \qquad (3)$$

If in these expressions we give τ different values, we get a series of values for W, ω, and a, corresponding to a series of configurations of the system, such configurations being stationary states in which there is no radiation of energy, and in which the electron will remain as long as the system is not disturbed from outside. We see that *the value of W is greatest if τ has its smallest value, viz. unity. This will therefore correspond to the most stable state of the system : i.e.* it will correspond to the binding of the electron for the removal of which the greatest amount of energy is required. Substituting in the above expressions $\tau = 1$, and $E = e =$ the charge on a single electron, and introducing the experimental values, *viz.* $e = 4{\cdot}7 \times 10^{-10}$, $e/m = 5{\cdot}31 \times 10^{17}$, $h = 6{\cdot}5 \times 10^{-27}$ we obtain :—

$$2a = 1{\cdot}1 \times 10^{-8} \text{ cm.}\ ;\ \omega = 6{\cdot}2 \times 10^{15} \text{ per sec.}\ ;\ W/e = 13 \text{ volt.}$$

We see that these values are of the accepted order of magnitude for the linear dimensions of the atoms, the optical frequencies, and the ionisation potentials respectively.

It is to be clearly borne in mind that the results so far obtained rest on two main hypotheses :—

1. That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary electro-dynamics, whilst the passage of the systems between different stationary states cannot be treated on that basis.

2. That the latter process is followed by the emission of homogeneous radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

The next problem which Bohr takes up is to show that his theory is capable of accounting for the line spectra of hydrogen.

If we consider the act of binding a free electron to a hydrogen nucleus carrying a positive charge equivalent to the charge on a single electron so that the electron finally rotates in one of the stationary states, the energy radiated out in the formation of this stationary state is given by equation (3), *viz.*—

$$W_\tau = \frac{2\pi^2 me^4}{h^2 \tau^2}.$$

The amount of energy emitted by the passing of the electron from a state where $\tau = \tau_1$ to a state where $\tau = \tau_2$ is consequently—

$$W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right).$$

The state corresponding to τ_2 is one in which the electron is closer to the nucleus than in the state corresponding to τ_1 ; in short, τ_2 is less than τ_1, and the linear dimension a of the atom is smaller when $\tau = \tau_2$ than when $\tau = \tau_1$.

If we now suppose that the radiation in question is homogeneous, and that the amount of energy emitted is equal to $h\nu$, we get—

$$W_{\tau_2} - W_{\tau_1} = h\nu$$

and hence

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right) \quad . \quad . \quad . \quad (4)$$

This expression gives the frequency of the homogeneous radiation emitted by the gas when the atomic system changes from the stationary state defined by τ_1 to the stationary state defined by τ_2. If these two states were the only possible ones the gas could only give rise to a single frequency ν. The quantities τ_2 and τ_1 are whole numbers, and a single atom is capable of existing in a corresponding number of stationary states, so that in general a number of lines will be emitted as is borne out by experiment. The above expression is capable of accounting for series of lines emitted by incandescent hydrogen. If we put $\tau_2 = 2$ and allow τ_1 to vary, *i.e.* τ_1 can take on the values 3, 4, 5, etc., we get the well-known Balmer series of lines in the hydrogen spectrum. It is noteworthy that to account for the Balmer hydrogen line spectra we have to assume that the electron from an outer orbit passes to the *second* orbit ($\tau_2 = 2$) and not to the first or innermost orbit, which represents maximum stability. If we put $\tau_2 = 3$ and allow τ_1 to vary ($\tau_1 = 4, 5, 6$, etc.), we get the infra-red series of lines observed by Paschen (*Ann. Physik*, **27**, 565 (1908)). If we put $\tau_2 = 1$ and allow τ_1 to vary we get a series in the extreme ultra-violet, the furthest Lyman region. In the case of elements heavier than hydrogen, *e.g.* platinum, the kind of radiation to be expected on putting $\tau_2 = 1$ corresponds to X-rays. If we put $\tau_2 = 4, 5$, etc., we get series of lines in the extreme infra-red not yet observed. It will be observed that Bohr's theory accounts excellently for those series of lines which have been observed in the case of hydrogen and is even capable of predicting other series in regions not yet examined. Further, the agreement is quantitative as well as qualitative. Putting $e = 4{\cdot}78 \times 10^{-10}$ electrostatic units; $e/m = 5{\cdot}31 \times 10^{17}$; and $h = 6{\cdot}55 \times 10^{-27}$, we get—

$$\frac{2\pi^2 me^4}{h^3} = 3{\cdot}26 \times 10^{15},$$

whilst the value obtained experimentally for the factor (the so-called Rydberg constant) outside the bracket in formula (4) is $3{\cdot}290 \times 10^{15}$. The agreement between the observed and calculated value is within the error due to experimental determination of the various quantities involved.

It may be pointed out that it has not been possible to observe more than twelve lines of the Balmer series in experiments with vacuum tubes whilst thirty-three lines are observed in the spectra of certain celestial bodies. This may likewise be anticipated on the basis of Bohr's theory. According to equation (3) the diameter of the orbit of the

electron in the different stationary states is proportional to τ^2. For $\tau = 12$, the diameter is equal to $1{\cdot}6 \times 10^{-6}$ cm., or equal to the mean distance apart of the molecules of a gas at a pressure of about 7 mm. of mercury; for $\tau = 33$ the diameter is equal to $1{\cdot}2 \times 10^{-5}$ cm., corresponding to the mean distance apart of the molecules at a pressure of about 0·02 mm. of mercury. According to the theory, the necessary condition for the appearance of a great number of lines is therefore a very small density of the gas, and if this were realised in a vacuum tube the whole mass of gas present would be insufficient to give rise to a measurable intensity of emission. In solar conditions we have large masses of incandescent gas at extreme rarefaction, and hence lines are observed under these conditions which cannot be observed in a vacuum tube.

Bohr next considers the spectrum of helium.

The neutral atom of helium consists, according to Rutherford, of a single positive nucleus of charge $2e$, with two electrons rotating in the same orbit around it. Now, considering the binding of a single electron by a helium nucleus, we get, on putting $E = 2e$, in expression (3)—

$$\nu = \frac{8\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right) = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\left(\frac{\tau_2}{2}\right)^2} - \frac{1}{\left(\frac{\tau_1}{2}\right)^2}\right).$$

If we put $\tau_2 = 1$ or $\tau_2 = 2$ in this formula we get series of lines in the extreme ultra-violet. If we put $\tau_2 = 3$ and let τ_1 vary we get a series of lines which includes two of the series observed by Fowler and ascribed by him to hydrogen. If we put $\tau_2 = 4$ we get the series observed by Pickering in the spectrum of ζ Puppis. Every second one of the lines of this series is identical with a line in the Balmer series of the hydrogen spectrum. It is not surprising therefore that these lines from ζ Puppis were ascribed to hydrogen. In Fowler's experiments hydrogen was mixed with helium in the vacuum tube. With helium alone in a vacuum tube the lines given by putting $\tau_2 = 3$ are not shown, as the ionisation of helium is so small. The presence of hydrogen appears to increase the ionisation of helium, due very probably to the fact that a positively charged hydrogen nucleus has a considerable affinity for electrons and consequently causes the helium atom to lose both of its electrons more easily than it would do in the absence of ionised hydrogen. The lines predicted by Bohr's theory refer to the binding of an electron by the helium nucleus which carries a positive double charge. Further, hydrogen atoms are known to be capable of acquiring a negative charge, so that their "catalytic" effect on the helium may be partly due to the affinity of neutral hydrogen atoms for electrons. Bohr explains in this manner a certain set of the lines obtained from a vacuum tube containing hydrogen and helium as due to the presence of the doubly charged helium nuclei combining with electrons. Finally, if we put $\tau_2 = 5$, 6, etc., in the above formula we get series, the strong lines of which are to be expected in the infra-red region.

We are now in a position to give something like a physical interpretation of Planck's constant h. Consider equation (2). If we denote the *angular momentum* of an electron rotating round a nucleus by M, it follows that for a circular orbit $\pi M = \frac{T}{\omega}$ where ω is the frequency of revolution and T the kinetic energy of the electron. For a circular orbit we further have T = W, as we have already seen. Hence—

$$M = \tau M_0$$

where $$M_0 = h/2\pi = 1{\cdot}04 \times 10^{-27}.$$

If we assume therefore that the orbit of the electron in the stationary state is circular we can say: the angular momentum of the electron round the nucleus in any one of the stationary states of the system is equal to an entire multiple of a universal value M_0 or $h/2\pi$, independent of the charge on the nucleus. The possible importance of the angular momentum in relation to Planck's theory has also been emphasised by Nicholson.

We can only observe a great number of different stationary states by investigating emission and absorption of radiation. In most of the other physical phenomena we deal with atoms in a single state, the state which corresponds to low temperatures. From these considerations we are led to the assumption that the permanent state is the one among the stationary states during the formation of which (from free electron and nucleus) the greatest amount of energy is emitted. According to equation (3) this state corresponds to $\tau = 1$.

As regards the process of absorption of radiation, the existence of Kirchhoff's law (*viz.* that a body absorbs radiation of the same wavelength as it emits), naturally suggests that the same mechanism is to be attributed to absorption as to emission, absorption taking place when an electron passes from an inner orbit to an outer.

Bohr's theory is likewise in agreement with Einstein's expression for the photo-electric effect, *viz.* $T = h\nu - W$, where T is the kinetic energy of the electron ejected under the influence of light of frequency ν, and W is the total amount of energy which would be emitted during the act of binding a free electron to the nucleus of the atom (*cf.* following chapter).

We have now to consider in more detail what has been called the permanent state of an atomic system. We have seen that in the case of a system consisting of a nucleus and a single electron, the permanent state is defined by the condition that the angular momentum of the electron is $h/2\pi$. The atom of hydrogen corresponds to this system, but the atom of hydrogen is difficult to deal with because of the very slight dissociation of gaseous molecular hydrogen. In order to get a closer comparison with experiment it is necessary to consider more complex systems. Let us consider a ring of n electrons rotating round a nucleus of charge E, the electrons being arranged at equal angular intervals round the circumference of a circle of radius a.

The total potential energy of the system consisting of the electrons and the nucleus is—

$$P = -\frac{ne}{a}(E - es_n) \quad . \quad . \quad . \quad . \quad (5)$$

where $$s_n = \frac{1}{4}\sum_{s=1}^{s=n-1} \operatorname{cosec} \frac{s\pi}{n}.$$[1]

[1] The above expressions require probably a little explanation. Let us consider a positively charged nucleus, charge E surrounded by n electrons, each of charge e, the electrons being arranged at equal distances on the circumference of a circle of radius a. We shall number the electrons 1, 2, 3, etc., up to n. The problem is to find the expression for the potential energy of this entire system, the potential energy being measured by the work which it is necessary to do upon the system in order to remove all the electrons to an infinite distance from the nucleus and from each other. First of all consider the nucleus with respect to electron 1. There is a force of *attraction* between the electron and the nucleus amounting to e_1E/a^2. The potential of the electron with respect to the nucleus being $-e_1E/a$, the minus sign being introduced because, in pulling the electron away, we *oppose* the natural direction in which the electron tends to move (*viz.* towards the nucleus). For electron 2 we have a similar term, so that for the n electrons we have the potential energy of the electrons with respect to the nucleus given us by the expression $-neE/a$. We have now to consider the effect of the electrons upon each other. The force is now one of repulsion. It therefore aids the process of pulling apart. The expression for the potential energy of each electron with respect to every other appears therefore with a positive sign. Consider electron 1, first of all with respect to electron 2. The force of repulsion is $e^2/r_1^2{}_{,2}$ where $r_{1,2}$ is the chord connecting the two electrons. The potential of electron 1 with respect to 2 is therefore $e^2/r_{1,2}$. The potential of electron 1 with respect to electron 3 is given by $e^2/r_{1,3}$ and so on up to the nth electron. The total potential energy due to the $(n-1)$ electrons acting upon electron 1 is thus given by a sum of $(n-1)$ terms:—

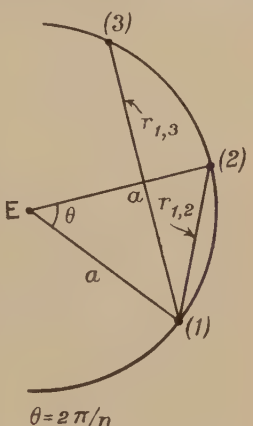

FIG. 10.

$$e^2/r_{1,2} + e^2/r_{1,3} + e^2/r_{1,4} + \ldots + e^2/r_{1,n}.$$

Now from the figure it is seen that—

$r_{1,2} = 2a \sin \pi/n$ where $2\pi/n$ is the angle between successive electrons.
$r_{1,3} = 2a \sin 2\pi/n$ " " " " "
$r_{1,4} = 2a \sin 3\pi/n$ " " " " "
$r_{1,n} = 2a \sin (n-1)\pi/n$ " " " "

Hence the sum of the potential energy terms of electron 1 with respect to all the others is—

$$\frac{e^2}{2a}[\operatorname{cosec} \pi/n + \operatorname{cosec} 2\pi/n + \operatorname{cosec} 3\pi/n + \ldots + \operatorname{cosec} (n-1)\pi/n].$$

For electron 2 we can write down an analogous set of terms and so on up to the nth electron. The sum of all such terms is therefore n times the series given. That is, for all electrons mutually acting upon one another we have—

$$\frac{ne^2}{2a}[\operatorname{cosec} \pi/n + \operatorname{cosec} 2\pi/n + \operatorname{cosec} 3\pi/n + \ldots + \operatorname{cosec} (n-1)\pi/n].$$

For the radial force exerted on an electron by the nucleus and the other electrons we get—

$$F = -\frac{1}{n}\frac{dP}{da} = -\frac{e}{a^2}(E - es_n) \quad . \quad . \quad . \quad (5a)$$

Denoting the kinetic energy of an electron by T and neglecting the electro-magnetic forces due to the motion of the electrons, we get on equating the centrifugal force on an electron to the radial force—

$$\frac{2T}{a} = \frac{e}{a^2}(E - es_n)$$

or

$$T = \frac{e}{2a}(E - es_n).$$

From this we get for the frequency of rotation—

$$\omega = \frac{1}{2\pi}\sqrt{\frac{e(E - es_n)}{ma^3}}.$$

The total amount of energy W which must be given to the system in order to remove the electrons to infinite distances apart from the nucleus and from each other is—

$$W = -P - nT = \frac{ne}{a}(E - es_n) - \frac{ne}{2a}(E - es_n) = \frac{ne}{2a}(E - es_n) = nT \quad . \quad (6)$$

But it is evident at once that in adding up all the terms which go to make up the above expression we have counted each potential term twice over. Thus, the potential between 1 and 3 appears when we are considering electron 1 by the term $e^2/r_{1,3}$. Similarly when we consider electron 3 with respect to the others we have amongst other terms the term $e^2/r_{3,1}$, which is simply the potential $e^2/r_{1,3}$ over again. Hence to get the true potential of all the electrons with respect to one another we have to divide the above expression by two. That is we get—

$$\frac{ne^2}{4a}[\text{cosec } \pi/n + \text{cosec } 2\pi/n + \text{cosec } 3\pi/n + \ldots + \text{cosec } (n-1)\pi/n].$$

Now the total potential P of the system is made up of terms due to the nucleus acting upon the electrons and the electrons acting upon one another. That is—

$$P = -\frac{nEe}{a} + \frac{ne^2}{4a}[\text{cosec } \pi/n + \text{cosec } 2\pi/n + \ldots + \text{cosec } (n-1)\pi/n].$$

If we now write the bracket in the form $\sum_{s=1}^{s=n-1} \text{cosec } s\pi/n$

and further write the symbol s_n for $\frac{1}{4}\sum_{s=1}^{s=n-1} \text{cosec } s\pi/n$

it follows that we can write—

$$P = -\frac{nEe}{a} + \frac{ne^2}{a}s_n$$

or

$$P = -\frac{ne}{a}(E - es_n)$$

which is the expression given by Bohr.

That is, the energy W is equal to the kinetic energy taken for a whole revolution of all the electrons when rotating in the stationary orbit. This is the same relation as holds for the case of a single electron rotating in an orbit. Notice also that the total potential energy P of the system is just double the kinetic energy of the electrons.

We see that the only difference in the above formula (6) and that holding for the motion of a single electron in a circular orbit round a nucleus is the exchange of E for $(E - es_n)$. We are therefore led to suppose that the kinetic energy per electron rotating in a stationary state is again $\tau h\frac{\omega}{2}$. The permanent configuration, that is, the configuration in the formation of which the maximum amount of energy is emitted, is the one for which $\tau = 1$. The angular momentum of each single electron in this state is again $h/2\pi$. Also, we can express angular momentum in all cases as mva where m is the mass of the rotating particle travelling with a velocity v round a circle of radius a. That is—

$$v = \frac{1}{a}\frac{h}{2\pi m} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

There may be many stationary states which a single ring of electrons may assume. This seems necessary to account for the line spectra of substances containing more than one electron per atom. Further there may be stationary configurations of a system of n electrons and a nucleus of charge E in which all the electrons are not arranged in a single ring.

As regards the stability of a ring of electrons, two problems arise. First as regards the stability for displacement of the electrons *in* the plane of the ring, and secondly, as regards displacements perpendicular to this plane. Nicholson has shown that the question of stability is very different in the two cases. While the ring for the latter displacements (displacements perpendicular to the ring) is in general stable, the ring is in no case stable for displacements in the plane of the ring. This conclusion is based upon classical electro-dynamics, and Bohr avoids the difficulty by making use of the quantum idea. In fact he shows that the stability of a ring of electrons rotating round a nucleus is secured through the condition of the universal constancy of the angular momentum $h/2\pi$ of each electron together with the further condition that the configuration of the electrons is that in the formation of which —from free electrons and nucleus—the amount of energy, W, emitted is a maximum; in other words, the stable configuration possesses the least energy. That this assumption leads to the condition for stability may be shown as follows.

Consider a ring of electrons rotating round a nucleus and let us assume that the system is in dynamical equilibrium, the radius of the ring being a_0, the velocity of the electrons v_0, their total kinetic energy T_0, and the total potential energy of the entire system P_0. We have already seen from equation (6) that $P_0 = -2T_0$. Next consider a

configuration of the system in which the electrons, under the influence of extraneous forces, rotate with the same angular momentum round the nucleus in a ring of radius a where $a = \alpha a_0$, α being greater than unity. In this case we have $P = \frac{1}{\alpha} P_0$ (as follows from the definition of potential energy given by equation (5)); also on account of the constancy of the angular momentum it follows that $v = \frac{1}{\alpha} v_0$ (compare equation (7)), and $T = \frac{1}{\alpha^2} T_0$, for T involves the square of v and therefore the square of a. It follows then that—

$$P + T = \frac{1}{\alpha} P_0 + \frac{1}{\alpha^2} T_0 = (P_0 + T_0) + T_0 \left(1 - \frac{1}{\alpha}\right)^2.$$

We see that the total energy (P + T) of the new configuration is greater than the $(P_0 + T_0)$ of the original configuration. The system is therefore stable for the displacement considered, that is it will tend to revert to the first configuration, for the first configuration corresponds to a maximum value of W as defined previously.

The condition of stability which we have just been considering refers to possible displacements of the electrons *in* the plane of the ring. It is necessary to consider the problem of stability in more detail however before we take up the problem of actual atoms containing several electrons.

Configuration and Stability in Systems Possessing one Nucleus.

Let us consider an electron of charge e and mass m moving in a circular orbit of radius a with a velocity v, which is small compared with the speed of light. Let us denote the radial force acting on the electrons by $\frac{e^2}{a^2} F_o$; F_o will be dependent in general upon a. The condition of dynamical equilibrium gives—

$$\frac{mv^2}{a} = \frac{e^2}{a^2} F_o.$$

Introducing the condition of universal constancy of the angular momentum of the electron we have—

$$mva = h/2\pi.$$

From these relations we get—

$$a = \frac{h^2}{4\pi^2 e^2 m F_o}; \text{ and } v = \frac{2\pi e^2 F}{h}$$

and for the frequency of revolution—

$$\omega = 4\pi^2 e^4 m F_o^2 / h^3.$$

If F^o is known, the dimensions and frequency of the corresponding orbit are determined by these equations.

We have seen already (equation (5*a*)) that the radical force F is given by—

$$F = -\frac{e}{a^2}(E - es_n)$$

where F is the force acting upon a single electron in a system containing n electrons, E being the charge on the nucleus. Now $E = Ne$, where N denotes the number of unit[1] charges carried by the nucleus. It follows therefore that—

$$F = \frac{e}{a^2}(Ne - es_n) = \frac{e^2}{a^2}(N - s_n).$$

But we have just seen that—

$$F = \frac{e^2}{a^2} \cdot F_o.$$

Hence $$F_o = (N - s_n).$$

Further, we have seen that the energy term, W, is given by—

$$W = -P/2 = \frac{ne}{2a}(E - es_n) = \frac{ne}{2a}(Ne - es_n) = \frac{ne^2}{2a}(N - s_n)$$

$$= \frac{ne^2}{2a}F_o.$$

W refers of course to all the electrons in the system. Further—

$$a = h^2/4\pi^2e^2mF_o.$$

Hence $$W = 2n\pi^2e^4mF_o^2/h^2.$$

If we now consider the simplest type of atom, *viz.* the hydrogen atom, the energy emitted, W_o, in bringing the single electron from infinity up to the most stable position is given by—

$$W_o = 2\pi^2e^4m/h^2$$

(compare equation (3), remembering that the most stable or permanent condition means that $\tau = 1$).

Hence for a system containing n electrons with nuclear charge Ne we can write—

$$W = W_o n F_o^2.$$

Also, for the simplest atom in its permanent state we have seen already (equation (3)) that—

$$a_o = h^2/4\pi^2me^2.$$

Hence for a system containing n electrons, the charge on the nucleus being Ne, we can write—

$$a = a_o/F_o; \text{ and } \omega = \omega_o F_o^2.$$

[1] The charge on a single electron being here regarded as the "unit" of (negative) electricity.

Using the numerical values already employed for the hydrogen atom we see that—

$$W_o = 2{\cdot}0 \times 10^{-11} \text{ erg.}$$
$$a_o = 0{\cdot}55 \times 10^{-8} \text{ cm.}$$
$$\omega_o = 6{\cdot}2 \times 10^{15} \text{ revolutions per second,}$$

and therefore, for the system containing n electrons and charge Ne on the nucleus—

$$W = 2{\cdot}0 \times 10^{-11} \times nF_o^2 \quad . \quad . \quad . \quad . \quad \text{(i)}$$
$$a = 0{\cdot}55 \times 10^{-8}/F_o \quad . \quad . \quad . \quad . \quad \text{(ii)}$$
$$\omega = 6{\cdot}2 \times 10^{15}F_o^2 \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

In order to use these expressions in actual calculation it is necessary to know F_o, *i.e.* $(N - s_n)$. Bohr gives the following table of values for s_n for various values of n up to $n = 16$. For $n = 1$, s_n is of course zero :—

n.	s_n.	Minimum Value of N.[1]	n.	s_n.	Minimum Value of N.
1	0	0	9	3·328	13·14
2	0·25	0·25	10	3·863	18·13
3	0·577	0·58	11	4·416	23·60
4	0·957	1·41	12	4·984	30·8
5	1·377	2·43	13	5·565	38·57
6	1·828	4·25	14	6·159	48·38
7	2·305	6·35	15	6·764	58·83
8	2·805	9·56	16	7·379	71·65

The numbers of electrons represented by n refer to the number of electrons in a single ring. This is in general a smaller number than that represented by N, for in a neutral atom N is necessarily equal to the total number of electrons present, some of which are present in the innermost ring, others in outer rings. We see from the table that the number of electrons which can rotate in a *single* ring round a nucleus of charge Ne increases only very slowly with increase in N ; for N = 20, the maximum value of n is 10 ; for N = 40, $n = 13$; for N = 60, $n = 15$. We see further that a single ring of n electrons cannot rotate in a single ring round a nucleus of charge ne unless n is less than 8. That is, if we consider an atom which has but one ring of electrons (and therefore $n = N$), the maximum number of electrons in this ring is 7. If more electrons be present at least two rings must be formed.

Hydrogen.

We have already considered the values of W, a, and ω (*i.e.* W_o, a_o, and ω_o) which satisfy the condition of stability for the electrically *neutral* atom of hydrogen. It is of interest, however, to consider the case of a

[1] Of course N cannot be fractional. The nearest whole number greater than the numbers quoted will give the smallest value for N.

negatively charged hydrogen atom, that is, one which has picked up an extra electron. In this case $n = 2$ and $N = 1$, for Ne = the nuclear charge = e in the case of the hydrogen nucleus. On substituting $n = 2$ and the corresponding value of s_n from the above table in the expressions (i), (ii), and (iii), we find that this system—which can be represented by the symbol **1**, (2), where (2) refers to the total number of electrons in the atmosphere and **1** refers to N, the number of unit charges on the positive nucleus—will give rise to a permanent state conditioned by the following values of a, ω, and W :—

$$a = 1{\cdot}33\ a_0;\ \omega = 0{\cdot}563\ \omega_0^-;\ W = 1{\cdot}13\ W_0.$$

Since W is here *greater* than it is when the atom is neutral, it follows that the hydrogen atom is actually capable of taking on a negative charge, for in doing so, the term W is increased from W_0 to $1{\cdot}13\ W_0$, and one of the conditions for stability is, as we have seen, a maximum value for W. The fact that the hydrogen atom can take on a negative charge probably accounts for the fact that in the periodic table we usually place hydrogen with the halogens partly because hydrogen can replace chlorine in organic compounds.

Bohr has also calculated the value of W which would result if the hydrogen atom acquired two extra electrons, thus becoming (**1**, (3)). It is found that W now becomes equal to $0{\cdot}54\ W_0$. This value of W is now less than W_0, its value for the neutral atom, and consequently still less than for the atom carrying one extra electron. Hence such a doubly charged hydrogen atom is unstable and will not exist. Experiments on positive rays show that the hydrogen atom can acquire a single negative charge, but it is doubtful if it can acquire a double negative charge.

Helium.

In this case $N = 2$, and the neutral atom has therefore two electrons. We have already considered Bohr's theory in relation to the spectrum of helium. We have now to take up the process whereby first one, then a second, and finally a third electron can be added to the doubly charged helium nucleus. First, for the formation of the system, (**2**, (1)), by bringing an electron from infinity up to the nucleus, since $n = 1$ and therefore $s_n = 0$, and further since $N = 2$, the permanent state is given by—

$$a = 0{\cdot}5\ a_0;\ \omega = 4\omega_0;\ W = 4W_0.$$

If we now bring the second electron up to the (**2**, (1)) system we find for the permanent state—since $s_n = 0{\cdot}25$ for n equal to 2—

$$a = 0{\cdot}571\ a_0;\ \omega = 3{\cdot}06\omega_0;\ W = 6{\cdot}13W_0.$$

Further, since

$$(W_{2,(2)} - W_{2,(1)}) = 2{\cdot}13W_0$$

it follows that each electron in a helium atom is more firmly held than the single electron in the hydrogen atom. It follows also that the ionisation potential of helium should be correspondingly high, as we would expect from the chemical inertness of helium. Bohr regards the two electrons of helium as being in the same ring.

If we now consider the process of adding an extra electron to the neutral helium atom so as to produce the configuration (**2**, (3)), it follows that the permanent state of the resulting system (since $s_n = 0{\cdot}577$ when $n = 3$) would be given by—

$$a = 0{\cdot}703a_0\,;\ \omega = 2{\cdot}02\omega_0\,;\ \mathrm{W} = 6{\cdot}07\mathrm{W}_0.$$

Since for this configuration W is less than it was for the neutral atom, the theory indicates that a helium atom cannot acquire a negative charge. This is in agreement with experiment, for Franck (*Ber. Deutsch. phys. Ges.*, **12**, 613 (1910)) has shown that helium atoms have no affinity for electrons.

Lithium.

In this case N = 3, the nuclear charge being $3e$. If one electron be brought up so as to form the system (**3**, (1)), *i.e.* an atom of lithium carrying effectively two positive charges, we get for the permanent state of the configuration (**3**, (1))—

$$a = 0{\cdot}33a_0\,;\ \omega = 9\omega_0\,;\ \mathrm{W} = 9\mathrm{W}_0.$$

If a second electron be brought up and enters the ring containing the first, the stable state for the resulting system (**3**, (2)) is—

$$a = 0{\cdot}364a_0\,;\ \omega = 7{\cdot}56\omega_0\,;\ \mathrm{W} = 15{\cdot}13\mathrm{W}_0$$

Since $\mathrm{W}_{3,\,(1)} = 9\mathrm{W}_0$, and since $(\mathrm{W}_{3,\,(2)} - \mathrm{W}_{3,\,(1)}) = 6{\cdot}13\mathrm{W}_0$, it follows that the first two electrons of the lithium atom are bound much more firmly than the electron of the hydrogen atom.

If we now consider the process of adding a third electron to the lithium nucleus so as to form a neutral atom, chemical considerations, *i.e.* considerations of valency, would suggest that the third electron should lie on a ring outside the ring containing the first two electrons, both rings being concentric. The single electron in the outer ring would be the valency electron of the lithium atom. The arrangement is represented by the symbol (**3**, (2) (1)), the large numeral indicating the nuclear charge. Proceeding as before, Bohr calculates that the stable state would correspond to the following:—

inner ring: $a_1 = 0{\cdot}362a_0\,;\ \omega_1 = 7{\cdot}65\omega_0$
outer ring: $a_2 = 1{\cdot}182a_0\,;\ \omega_2 = 0{\cdot}716\omega_0\,;\ \mathrm{W} = 16{\cdot}02\mathrm{W}_0.$

Since $(\mathrm{W}_{3,\,(2)\,(1)} - \mathrm{W}_{3,\,(2)}) = 0{\cdot}89\mathrm{W}_0$, we see that the outer electron of the neutral atom is less firmly held than the electron of the hydrogen atom.

For a negatively charged lithium atom, *i.e.* the configuration (**3**, (2)

(2)) we would have $W = 16{\cdot}16W_0$. This large value of W would suggest that negatively charged lithium might under certain circumstances manifest itself.

Bohr also considers beryllium, but enough has been said in connection with light atoms, in which the number of electrons is small, to indicate the line of reasoning.

We have now to consider the question of series of rings present in neutral atoms which contain a considerable number of electrons.

These rings are regarded as co-axial, lying in the same plane. Bohr calculates that only in the case of systems containing a very large number will there be any tendency for the rings to separate into different planes. It is unnecessary to discuss this case. Considering systems of rings in the same plane Bohr is led to important conclusions regarding the maximum number of electrons which can rotate in a single ring. We have dealt with this point earlier. It must be pointed out, however, that the value for n simply gives us the maximum number of electrons which could exist in a stable single ring; it does not follow that this number is reached in actual atoms. The formation of a second or of a third ring is possible, even when the nuclear charge does not exceed $8e$, *i.e.* when the total number of electrons does not exceed 8. The possibility of this becomes clear when we take into account the question of valency, for valency will be due essentially to the external ring. Bohr further shows that in the stable system the number of electrons in any ring diminishes as we proceed outwards from the nucleus. In dealing with actual atoms Bohr makes use of the now generally accepted relation (which will be discussed later), that the atomic number gives us directly the number of electrons in the atom. The atomic number of an element represents the position of the element in the whole series of elements, arranged in order of increasing atomic weight. It has been found that the atomic number, and consequently the number of electrons present in an atom is approximately one half of the atomic weight, *i.e.* helium 2, lithium 3, beryllium 4, oxygen 8, and so on.

It has already been stated that considerations of valency are a guide to the number of electrons in the outermost ring. For monovalent atoms the number is unity and so on for other atoms. A different consideration also enters into the problem, *viz.* the possibility of confluence of rings, especially when a considerable number of electrons are present.

Two rings may run together to form a single ring, and Bohr shows that this will occur most easily when the two rings contain the same number of electrons. Considering the binding of successive electrons by a positive nucleus we conclude from this that, unless the charge on the nucleus be very great, rings of electrons will join together if they contain the same number of electrons and rotate in the same direction, and that accordingly the number of electrons in inner rings will be the numbers, 2, 4, 8, 16, etc. This assumption in regard to the number of electrons in the rings is strongly supported by the fact that the chemical properties of the elements of low atomic weight vary with a period of eight. Further, it follows that the number of electrons on the outermost

ring will always be odd or even according as the total number of electrons in the atom is odd or even. This suggests a relation with the fact that the valency of an element of low atomic weight is always odd or even according as the number of the element in the periodic series is odd or even.

The fact that several considerations have been introduced into the problem shows that the criterion of stability—constancy of angular momentum and a maximum value for W—is not sufficient to determine completely the constitution of an atomic system. In very simple cases the constitution of the atom is in relatively little doubt. It is possible, however, by making use of all the foregoing considerations to arrive at a moderately satisfactory statement of the constitution of atoms which contain up to twenty-four electrons, that is, up to an atomic weight of forty-eight approximately. Bohr gives the following table for these atomic systems. The large numeral indicates the value of N, the total number of electrons in the neutral atom, whilst the smaller figures in brackets give the composition of the rings starting from the innermost.

Thus the symbol **9** (4, 4, 1) denotes a neutral atom which contains in all nine electrons, arranged in three concentric rings, the innermost ring containing four electrons, the second likewise four, and the outermost one electron, thereby indicating that the normal valency of this atom is one. The atomic weight of the element in question is approximately $2 \times 9 = 18$, *i.e.* fluorine. It will be observed that Bohr places hydrogen along with the halogens, and not with the alkali metals. Bohr does not give the name of the corresponding element to these configurations but the attempt is here made to do so.

TABLE SHOWING STRUCTURE OF ATOMS.

Probable Element.	Structure of Atom.	Probable Element.	Structure of Atom.	Probable Element.	Structure of Atom.
Hydrogen	**1** (1)	Fluorine .	**9** (4, 4, 1)	Chlorine .	**17** (8, 4, 4, 1)
Helium .	**2** (2)	Neon .	**10** (8, 2)	Argon .	**18** (8, 8, 2)
Lithium .	**3** (2, 1)	Sodium .	**11** (8, 2, 1)	Potassium	**19** (8, 8, 2, 1)
Beryllium	**4** (2, 2)	Magnesium	**12** (8, 2, 2)	Calcium .	**20** (8, 8, 2, 2)
Boron .	**5** (2, 3)	Aluminium	**13** (8, 2, 3)	—	**21** (8, 8, 2, 3)
Carbon .	**6** (2, 4)	Silicon .	**14** (8, 2, 4)	—	**22** (8, 8, 2, 4)
Nitrogen	**7** (4, 3)	Phosphorus	**15** (8, 4, 3)	—	**23** (8, 8, 4, 3)
Oxygen .	**8** (4, 2, 2)	Sulphur .	**16** (8, 4, 2, 2)	—	**24** (8, 8, 4, 2, 2)

Elements in the same horizontal line belong to the same group, the vertical columns indicate the first three periods of the elements.

As regards elements of higher atomic weight, Bohr points out that at the end of the third period of eight elements we meet with the iron group, which takes a particular position in the system of elements since it is the first time that elements of neighbouring atomic weights show similar chemical properties. This circumstance indicates that the configurations of the electrons in the elements of this group differ only in

the arrangement of the *inner* electrons. The fact that the period in the chemical properties of the elements after the iron group is no longer eight but eighteen suggests that elements of higher atomic weight contain a recurrent configuration of eighteen electrons in the innermost rings. The deviation from 2, 4, 8, 16 may be due to a gradual interchange of electrons between the rings as already indicated when speaking of the confluence of rings. Since a single ring of eighteen electrons will not be stable, the electrons may be arranged in two parallel rings. Such a configuration of the inner electrons will act upon the outer electrons in very nearly the same way as a nucleus of $(N - 18) \times e$. It is conceivable that with increase in N another configuration of the same type will be found outside the first, such as is suggested by the presence of a second period of eighteen elements.

Systems Containing Several Nuclei. Molecules.

According to Bohr a simple molecule such as the molecule of hydrogen consists of two positively charged nuclei, each carrying unit charge with a ring of two electrons rotating between them, the rotation being round the line joining the two nuclei. If the two nuclei are similar in all respects the electron ring rotates at a position midway between the nuclei, the plane of the ring being perpendicular to the line joining the nuclei. If the nuclei be dissimilar the ring will rotate at some position lying nearer the heavier and more complex nucleus.

The equilibrium of such a system is conditioned as before by the constancy of the angular momentum of each electron, along with the further condition that W—the energy emitted in binding an electron to the system—is a maximum.

Consider a system consisting of two positive nuclei of equal charges and a ring of electrons rotating round the line joining the nuclei. Let the number of electrons be n, the charge on each be e, and the charge on each nucleus be Ne. It can be shown that the system will be in equilibrium if (1) the nuclei are equidistant from the ring and (2) if the ratio between the diameter of the ring, $2a$, and the distance apart of the nuclei, $2b$, be given by—

$$b = a\left(\left(\frac{4n}{N}\right)^{2/3} - 1\right)^{-\frac{1}{2}} . \quad . \quad (8)$$

It is assumed that the frequency of revolution ω is a magnitude such that for each electron the centrifugal force balances the radial force (due to the attraction of the nuclei and the repulsion of the electrons). Denoting this radial force by $\frac{e^2}{a^2}F_o$ we get from the condition of the universal constancy of the angular momentum of the electrons as already shown—

$$a = \frac{h^2}{4\pi^2 e^2 m F_o}; \quad \omega = \frac{4\pi^2 e^4 m F_o^2}{h^3} \quad . \quad . \quad . \quad (9)$$

and W = total energy necessary to remove all the charged particles to infinite distances from one another $= \frac{2n\pi^2 e^4 m F_o^2}{h^2}$ . . . (10)

For the system in question we have—

$$F_o = \frac{N^2}{2n}\left(\left(\frac{4n}{N}\right)^{2/3} - 1\right)^{3/2} - s_n \quad . \quad . \quad (11)$$

where s_n has its former significance. It will be observed that F_o is a function of the radius of the ring.

As regards the stability of the ring of electrons with respect to displacements *perpendicular* to the plane of the ring, Bohr shows that the system will not be stable unless when N = 1, n = 2 or 3. Throughout the entire treatment of the problem it will be observed that Bohr regards the question of stability with respect to such "perpendicular" displacements as being capable of being dealt with by classical electrodynamics. In the case of displacements of electrons *in* the plane of the ring classical electrodynamics is incapable of indicating any position of stability, and Bohr finds the condition by introducing the quantum theory in the form of the constant angular momentum ($h/2\pi$) possessed by each electron in whatever orbit it may be rotating.

It is assumed that the motions of the nuclei with respect to one another are so slow that the state of motion of the electrons at any moment will not differ sensibly from that calculated on the assumption that the nuclei are at rest. This assumption is permissible on account of the great mass of the nuclei compared with that of the electrons, which means that the vibrations resulting from a displacement of the nuclei are very slow compared with those resulting from a displacement of the electrons.

Let us now imagine that, by the help of extraneous forces acting on the nuclei, we slowly alter the distance between them. During this displacement the radius of the ring of electrons will alter in consequence of the alteration in the radial force due to the attraction of the nuclei for the electrons. During this alteration we suppose that the angular momentum of the electrons remains constant. If the distance apart of the nuclei increases, the radius of the electron ring will likewise increase. It can be shown, however, that the radius of the ring will increase at a slower rate than does the distance between the nuclei. On account of this difference in the rate the attraction on one of the nuclei due to the ring will be greater than the repulsion from the other nucleus. The work done during the displacement by the extraneous forces acting upon the nuclei will therefore be positive, and the system will be stable for this displacement. The same result will also hold in the case in which the distance between the nuclei diminishes.

For a system consisting of a ring of electrons and two nuclei of *unequal* charge the investigation becomes more complicated. During a variation of the distance of the nuclei apart not only will the radius of the electron ring vary, but also the ratio in which the plane of the ring

divides the line connecting the nuclei. If we consider a neutral system, containing two nuclei carrying *large* charges, in the stable configuration the greater part of the electrons must be arranged round each nucleus, approximately, as if the other nucleus were absent; and only a few of the outer electrons will be arranged differently, rotating in a ring round the line connecting the nuclei. This ring which keeps the system together represents the chemical bond.

Systems Containing Few Electrons; the Hydrogen Molecule.

As already stated, the neutral hydrogen molecule consists of two similar nuclei each carrying unit charge e with two electrons rotating in a ring between the nuclei. Denoting the radius of the ring by a, and the distance apart of each nucleus from the plane of the ring by b, we get from equation (8), on putting $N = 1$, and $n = 2$—

$$b = a/\sqrt{3}.$$

From (11) we get further—

$$F_0 = 3\frac{\sqrt{3} - 1}{4} = 1{\cdot}049.$$

From (9) and (10) we get—denoting the values of a, ω, and W for a system consisting of a single electron and single nucleus (*i.e.* the hydrogen atom) by a_0, ω_0, and W_0—the following values for the hydrogen molecule:—

$$a = 0{\cdot}95a_0; \quad \omega = 1{\cdot}10\omega_0; \quad W = 2{\cdot}20W_0.$$

Since W is greater than $2W_0$, it follows that two hydrogen atoms combine to form a molecule with emission of energy. That is a hydrogen molecule dissociates with absorption of energy. This is in agreement with experiment. Putting $W_0 = 2{\cdot}0 \times 10^{-11}$ erg, and $N_0 = 6{\cdot}2 \times 10^{23}$, where N_0 is the number of molecules in one gram-molecule, we get for the energy emitted during the formation of one gram-molecule of hydrogen from two gram-atoms, the quantity $N_0(W - 2W_0) = 2{\cdot}5 \times 10^{12}$ erg, or 60,000 cals. This value is of the correct order of magnitude, the value observed by Langmuir being approximately 80,000 cals.

In considering displacements of electrons perpendicular to the plane of the ring, we have seen that the molecule will become unstable unless when $N = 1$, $n = 2$ or 3. Hence if we remove one of the two electrons from the hydrogen molecule the whole system will become unstable and will break up into a single nucleus positively charged and a neutral hydrogen atom. This process corresponds to the change from a stationary state represented by the complete neutral molecule and a second stationary state represented by the dissociated molecule. On Bohr's theory when such a change takes place from one stationary to another there is involved homogeneous radiation of frequency ν, the

energy per molecule "decomposed" being $h\nu$. In this case $h\nu$ represents energy absorbed given by the relation—

$$h\nu = W - W_o = 1{\cdot}20W_o.$$

Hence $$\nu = 3{\cdot}7 \times 10^{15}.$$

The value for the frequency in the farthest ultra violet calculated from dispersional measurements in the case of hydrogen is $3{\cdot}5 \times 10^{15}$, so that the agreement is good. It may be pointed out that the "chemical" process involved in the above is $H_2 \rightarrow H + H^+ + \ominus$ It is not clear why this process should be identified with the dispersional frequency.

The above calculation refers to the quantum involved in adding or removing an electron. We have now to consider the frequency and consequent magnitude of the quantum involved if one nucleus is removed from the other. Bohr shows that this frequency is given by—[1]

$$\nu_r = 1{\cdot}32\omega^o\sqrt{\frac{m}{M}}$$

where m is the mass of an electron and M the mass of the nucleus. Putting $M/m = 1835$ and $\omega_o = 6{\cdot}2 \times 10^{15}$, we get—

$$\nu_r = 1{\cdot}91 \times 10^{14},$$

or $\lambda_r = 1{\cdot}57\mu$, *i.e.* the short wave-length region of the infra-red spectrum. This frequency is of the same order of magnitude as that calculated for the nuclear or atomic vibration of hydrogen on the basis of molecular heat (*cf.* Chap. IV.). On the other hand, no absorption of radiation in hydrogen gas corresponding to this frequency is observed. According to Bohr this is to be expected on account of the symmetrical structure of the hydrogen molecule and the great ratio between the frequencies corresponding to the displacements of the electrons and the nuclei respectively.

A system of two nuclei, each of charge e, and a ring of 3 electrons rotating between them—that is, a negatively charged hydrogen molecule —will be stable for displacements perpendicular to the ring, for the system is stable if $N = 1$ and $n = 2$ or 3. Bohr calculates that for such a system—

$$a = 1{\cdot}14a_o;\ \omega = 0{\cdot}77\omega_o;\ W = 2{\cdot}32W_o.$$

Since the W is greater in this case than it is in the case of the neutral hydrogen molecule ($W = 2{\cdot}20W_o$), the negatively charged molecule should be capable of existence. Proof of the existence of negatively charged hydrogen molecules has been obtained by Sir J. J. Thomson in experiments on positive rays (*Phil. Mag.*, **24**, 253 (1912)).

We have now to consider the mechanism whereby a molecule of hydrogen is formed from its constituents. We shall restrict ourselves to the union of two neutral hydrogen atoms. Suppose that two such

[1] This expression obtained by Bohr is obviously the same as that found by Haber in 1911 and referred to in the following chapter.

atoms are approaching one another at a rate which is sufficiently slow that the dynamical equilibrium of the electrons for every position of the nuclei is the same as if the latter were at rest. Suppose that the electron of atom 1 is rotating in the same plane as that of atom 2, the difference in phase being one-half of a revolution. During the approach, the direction of the planes of the orbits of the electrons and the difference in phase will be unaltered. The planes of the orbits will, however, at the beginning of the process approach each other at a higher rate than do the nuclei, for two electrons rotating in the same direction attract one another. Finally, at a certain distance of the nuclei apart the electron planes will coincide, the two electrons being now arranged in a single ring. During the further approach of the nuclei the *ratio* between the diameter of the electron ring and the distance apart of the nuclei will increase,[1] and the system will pass through a configuration in which it will be in equilibrium without the application of extraneous forces on the nuclei. That is, a permanent neutral hydrogen molecule is formed.

Now let us suppose that we are dealing with two helium atoms, *i.e.* systems consisting of a nucleus of charge $2e$ surrounded by a ring of two electrons, and let us imagine the above process repeated. Assume that at the beginning the helium atoms are orientated to each other like the hydrogen atoms, with the exception that the electrons in the helium atoms differ by one-quarter of a revolution instead of one-half. The planes of the electrons will again approach one another at a higher rate than do the nuclei, and for a certain position of the latter the planes will coincide. During the further approach of the nuclei, the 4 electrons will be arranged at equal angular intervals in a single ring. As in the former case it may be shown that at any moment during this operation the system will be stable for a displacement of the electrons perpendicular to the plane of the ring. Contrary, however, to what took place in the case of hydrogen, the extraneous forces to be applied to the nuclei in order to keep the system in equilibrium will always be in a direction to diminish the distance apart of the nuclei, and the system will never pass through a position of equilibrium. The helium atoms will in fact repel one another and no molecule will be permanently formed.

As regards molecular systems containing a considerable number of electrons the treatment becomes much more complicated. Bohr attempts to deal with such cases, and for details his paper must be consulted. It may be mentioned that, following an approximate method of calculation, Bohr is led to expect an absorption band in the infra-red spectrum of hydrochloric acid gas at $\nu = 13{\cdot}7 \times 10^{13}$ whilst the observed band lies at $\nu = 8{\cdot}5 \times 10^{13}$.

Bohr regards the water molecule as consisting of an oxygen nucleus surrounded by a ring of four electrons, and the two hydrogen nuclei situated on the axis of the ring at equal distances apart from the oxygen

[1] Of course the actual diameter of the electron ring diminishes but not so fast as does the distance between the nuclei.

nucleus and kept in equilibrium by two rings of greater radius than the one just mentioned, each of these two rings containing 3 electrons; the latter rotate in parallel planes round the axis of the system and are situated relatively to each other in such a way that the electrons in the one ring are opposite the intervals between the electrons in the other. If we imagine such a system broken up by slowly removing the hydrogen nuclei we should obtain two positively charged hydrogen atoms and an oxygen atom with a double negative charge in which the outermost electrons will be arranged in two rings of three electrons each, the two rings being parallel to one another.

Parson's Magneton and the Structure of the Atom.

Hitherto, in dealing with the problem of atomic structure, we have regarded the electron as a minute discrete particle of electricity or matter, assumed to be spherical, and capable of movement "inside" the atom in certain orbits, the velocity of movement being relatively small compared with the velocity of light. A new concept has been introduced, however, in connection with the electron which must be very briefly discussed. According to this view the electron itself is a tiny ring or annulus carrying a negative charge. The ring is regarded as rotating continuously with a peripheral velocity which is of the same order as that of light. This is equivalent to a circuit current, analogous to the Ampère currents assumed to account for magnetism, and consequently such a structure possesses magnetic properties. For this reason, A. L. Parson, to whom this concept of the electron is due (*Smithsonian Inst. Pub.*, **65**, No. 11, 1915), substitutes the word *magneton* in place of electron.

The term magneton was first introduced by Weiss in 1911 (*cf.* N. Campbell's *Modern Electrical Theory*). On the basis of the electron theory of paramagnetism an expression has been deduced for the *susceptibility* according to which this quantity should be proportional to M^2/T, where M is the magnetic moment of a molecule and T is the absolute temperature. Weiss observed that in the case of magnetite over a certain temperature range the curve connecting the susceptibility with the reciprocal of the temperature was not a straight line through the origin, as it should have been, but consisted of a series of lines separated by definite differences in the value of the susceptibility. This was ascribed by Weiss to abrupt, discontinuous variations in the value of the molecular magnetic moment M, and Weiss further showed that the various observed values were all even multiples of a certain quantity to which he gave the name the magneton. The magnitude (*i.e.* the moment) of the magneton is the same as that which would be produced by a rotating electron revolving in an orbit of radius 10^{-8} cm. with a frequency of 10^{14} per second approximately. Weiss of course kept to the classical concept of the electron.

In the case of Parson's ring electron or circuit current the radius of the ring is estimated to be about $1{\cdot}5 \times 10^{-9}$ cm., that is a quantity

somewhat less than the accepted value for the diameter of an atom. Parson's theory of atomic structure based upon the magneton hypothesis may be summarised as follows :—

The positive charge in the neutral atom, which must be present to balance the negative charges of the magnetons is regarded as a sphere of uniform positive electrification possessing a volume which is proportional to the number of magnetons which it contains. That is, the distribution of the positive charge is once more treated as in the original theory of atomic structure first advanced by Sir J. J. Thomson (*cf.* Chap. I., Vol. I.). This positive sphere is regarded as having the properties of an elastic solid and " is surrounded by an atmosphere or envelope of very low charge density which is also elastic ". Given this distribution, Parson shows that a group of eight magnetons may be arranged symmetrically round the sphere so as to give a stable configuration; and even with atoms possessing a larger number of magnetons, a similar distribution of eight is assumed. Such an arrangement obviously recalls the Abegg-Bodländer theory of valency, according to which the natural number of valencies is eight, though all these are not effective as far as another atom is concerned. To explain the existence of the long periods in the period classification as well as the properties of certain elements contained therein, it is necessary to assume a certain " hindrance " to the formation of the normal number of eight magnetons.

On the basis of these assumptions Parson discusses the single magnetic attraction between two such magnetons, the tendency to form the group of eight, the residual valency effect and the electrical polarisation set up by a magneton of the above type. On the basis of this atomic structure Parson has made a rough calculation of the heat of dissociation of hydrogen, obtaining the value 135,000 cals. per gram-molecule; Langmuir's value being of the order 80,000 cals.

One of the most obvious advantages of the Parson magneton is that it affords a rational basis for the assumption made by Bohr, *viz.* that an electron rotating in a stable orbit does not radiate. A rotating electron—as hitherto envisaged—suffers an effective inward acceleration in rotating, and hence, on the basis of the classical electromagnetic theory, it should emit radiation continuously, its orbit becoming smaller until it falls into the centre of the atom. On the basis of the classical electromagnetic theory it is also known that the greater the number of electrons rotating in a ring the less the radiation from the ring. The Parson ring magneton is equivalent to a continuous series of charges, and consequently such a ring, howsoever great its velocity, will not radiate at all. This carries out Bohr's idea of the absence of radiation from an electron *in* an orbit.

On the other hand one of the most obvious disadvantages of Parson's theory of atomic structure lies in the assumption of a uniform positive sphere of electricity, for on such a basis it is quite impossible to account for the large angle scattering of α rays observed by Rutherford. The point is therefore whether we can retain the advantage of the ring electron or magneton and at the same time get rid of the hypothesis of

the positive sphere, by substituting for it the nucleus idea of Rutherford. The difficulty, as already pointed out, consists in the fact that an atom consisting of a nucleus surrounded by an atmosphere of magnetons would be an unstable system. The problem has been discussed in a preliminary manner by D. L. Webster (*J. Amer. Chem. Soc.*, **40**, 375, 1918).

From what has been said it will be obvious that the magneton theory of atomic structure as developed by Parson is still in a rudimentary stage. Its advantages, however, are such, particularly in regard to its applicability to chemical phenomena, that it cannot be discarded without a serious attempt being made to overcome the main difficulty of the scattering of the α particles.

High Frequency Spectra of the Elements. Moseley's Relation.

By the high frequency spectrum is meant the X-ray spectrum which is obtained from a substance by bombarding the substance with β-rays. It has been pointed out in Vol. I., Chap. II., that the investigation of the structure of crystals by means of their X-ray spectra affords a means of determining with precision the wave-length of any homogeneous X-ray employed. X-rays only differ from light in possessing very much shorter wave-lengths (of the order 10^{-8} cm.). The substance to be used as a source of X-rays forms the anticathode in a vacuum tube, and the beam of X-rays emitted as a result of bombardment by the cathode rays is characteristic of the substance forming the anticathode. In general the X-rays thus excited are not homogeneous. They consist of two or more wave-lengths which can be analysed and measured by means of the crystal acting as a grating. As a rule, however, one frequency is more prominent than the others, that is, the intensity of the resulting spectrum is greatest for one type, and for the sake of simplicity we shall consider these single frequencies as characteristic of the X-rays emanating from the substance examined. When the anticathode is of nickel, the characteristic wave-length of the X-ray produced is $1{\cdot}10 \times 10^{-8}$ cm. It follows, therefore, that a single quantum $h\nu$ of this type contains energy in amount $1{\cdot}78 \times 10^{-8}$ ergs. It is of interest to compare this quantity with the energy of the electron of the cathode stream which gave rise to the X-ray. Whiddington (*Proc. Camb. Phil. Soc.*, 1910) has shown that an electron of the cathode stream will not excite X-ray radiation unless its velocity exceeds a certain critical value, which varies with the nature of the material composing the anticathode. If the latter be of nickel the limiting velocity of the electron striking it is $6{\cdot}17 \times 10^{9}$ cm. per sec., or about one-fifth of the speed of light. Taking the mass of the electron to be $0{\cdot}9 \times 10^{-27}$ gram, the kinetic energy of the electron possessing the limiting speed is $1{\cdot}7 \times 10^{-8}$ erg, a quantity which is very nearly the same as the energy in a single quantum of the X-ray produced. Further, the investigation of the reverse process, *i.e.* the emission of an

electron by means of X-rays, has shown that the kinetic energy of the electron is approximately equal to that of the cathode ray which excited the X-ray in the first instance. As Bragg remarks "we are justified in assuming that these processes are actual examples of the give-and-take of radiant energy with which Planck's hypothesis is concerned".

Whiddington has also found that the limiting velocity of an electron just necessary to excite an X-ray from a particular element is proportional to the atomic weight of the element. Now we have seen that the frequency ν of the X-ray is proportional to the kinetic energy of the electron producing the ray. Hence the frequency of the X-ray is proportional to the square of the velocity of the electron and therefore to the square of the atomic weight. This serves as a useful guide in the choice of a substance for the anticathode which will produce an X-ray of a given kind.

In 1913 van den Broek (*Physikal. Zeitsch.*, **14**, 32) suggested, that in comparing elements with one another, the atomic number, that is, number which represents the position of the element in the periodic table is a far more fundamental quantity than the atomic weight itself. As a matter of fact the atomic number of an element is approximately one-half of the atomic weight, so that any quantity proportional to the atomic weight is likewise proportional to the atomic number.

The connection between the nature of an element and the frequency of the X-ray produced from it has been systematically studied by Moseley (*Phil. Mag.*, [vi.], **26**, 1024; *ibid.*, **27**, 703 (1914)). On plotting the square root of the frequency of the X-ray produced from a given element against the atomic number of the element, for a whole series of elements, Moseley found that a simple linear relation connected the two quantities. This was true both for the K and L types of X-rays, types which differ from one another in intensity, the K type being produced from a "hard" bulb (high vacuum), the L type being produced from a "soft" bulb. It is evident that the atomic number is not simply an ordinal but possesses some actual physical significance. The Rutherford atom-model, already discussed, suggests what this significance is.

The measurements of Rutherford and Geiger showed that the magnitude of the positive charge on the nucleus was Ne where e is identical with the magnitude of the charge on an electron, and N is a number approximately one-half the atomic weight. N is in fact a number identical with the atomic number. It is probable that the elements differ from one another in the magnitude of the nuclear charge, and it is reasonable to suppose that successive elements in a table of elements vary by the amount e on the nuclear charge. Regarding the nuclear charge of hydrogen atom as e itself, the succeeding elements will possess $2e$, $3e$, and so on, or in other words, the *atomic number indicates the magnitude of the nuclear charge*. If this be so, the various relations found between atomic number and other quantities serves to relate these quantities to the magnitude of the nuclear charge. The simplest form of Bohr's

relation, already discussed, between the frequency of emitted radiation and electronic charge involves the square of the latter. In other words, the square root of the frequency emitted is proportional to e itself. Bohr's relation, in fact, is capable of predicting the characteristic X-ray radiation from an element of high atomic weight with considerable exactness. In this connection it may be pointed out (*cf. Millikan Physical Review*, Aug., 1917) that the orbit of the innermost electron is inversely proportional to the atomic number or nuclear charge, *i.e.* the greater the charge on the nucleus the smaller the radius of circular path followed by the innermost electron.

Characteristic Infra-red Frequency and Atomic Number.

An interesting relationship has been pointed out by Allen (*Proc. Roy. Soc.*, **A**, **94**, 100 (1917)) between the atomic number and the infra-red frequency which accounts approximately for the atomic heat of the element. Writing N for the atomic number and ν for the frequency of a given element, Allen's relationship is—

$$N\nu = n\nu_A$$

where n is an integer called the frequency number, and ν_A is a fundamental constant the same for all elements. The mean value for ν_A is $21{\cdot}3 \times 10^{12}$. The following table illustrates the above relation. The experimental values of ν for the various elements (obtained from atomic heat measurements of Nernst, Griffiths, and Keesom-Onnes) have been multiplied by the atomic number N.

Element.	N.	$N\nu \times 10^{-12}$.			Mean.
		Nernst.	Griffiths.	Keesom-Onnes.	
Al . . .	13	5 × 21·6	5 × 21·4	—	5 × 21·5
Fe . . .	26	—	10 × 20·9	—	10 × 20·9
Cu . . .	29	9 × 21·3	9 × 21·9	9 × 21·2	9 × 21·3
Zn . . .	30	7 × 20·6	7 × 20·6	—	7 × 20·6
Ag . . .	47	10 × 21·2	10 × 21·1	—	10 × 21·1
Cd . . .	48	—	8 × 21·1	—	8 × 21·1
Hg . . .	80	8 × 20·2	—	—	8 × 20·2
Pb . . .	82	7 × 22·2	7 × 22·5	7 × 21·6	7 × 22·0

The above relationship is empirical and its full significance has not yet been determined. It may be pointed out, however, that Biltz has shown the characteristic infra-red frequency ν of the elements to be a periodic function of the atomic weight, and therefore of the atomic number. Since ν_A is a constant it follows that n must likewise vary in a periodic manner with the atomic weight or number. This is not the same thing, however, as explaining the significance of n.

CHAPTER VI.

(Systems not in equilibrium)—Quantum theory and the photo-electric effect—Photochemical reactions—Einstein's Law of the photochemical equivalent—Thermal reactions—Reaction velocity from the standpoint of the quantum theory.

The Photo-electric Effect.

Hallwachs in 1888 was the first to show that a body carrying a charge of negative electricity loses its charge on being exposed to ultra-violet light; on the other hand a positively charged body is not discharged. Later, Hallwachs and Righi showed, independently, that an insulated metal exposed to ultra-violet light acquires a positive charge. That is to say, negatively charged particles, electrons, are emitted from the metal under the action of ultra-violet light. This phenomenon is known as the photo-electric effect. Certain metals, such as the alkali metals and zinc and aluminium, exhibit this effect even under the influence of ordinary "visible" light, the effect being greatest in the case of the alkali metals. It is essential in all these cases that the surface should be fresh and clean; if a layer of oxide forms, the effect is greatly weakened. This is known as photo-electric fatigue.

This emission of electrons is bound up with an absorption of the light. The periodic electric force in the radiation sets the electrons on the surface into more violent vibration, so that some of them are ejected from the metal into the neighbouring space. If v is the velocity possessed by an ejected electron, its kinetic energy is $\frac{1}{2}mv^2$, where m is the mass of the electron. If the surface be charged positively to a potential of V volts, which potential is just able to prevent the escape of the electron, it follows that Ve, where e is the charge on the electron, is just equal to $\frac{1}{2}mv^2$, *i.e.* the kinetic energy which the electron would have had if no potential had existed.

Experiment has shown that the photo-electric effect really comprises two phenomena, *apparently* distinct from one another. These are known as the *normal photo-electric effect* and the *selective photo-electric effect* respectively. We shall consider the normal effect in the first place.

The photo-electric current, produced by the moving electrons which have been set free from the surface, depends upon two factors, (1) the *number* of electrons emitted in unit time, and, (2) the *speed* of these electrons. If the intensity of the light be increased, without altering the colour or quality (*i.e.* without altering the vibration frequency), it

has been found that the photo-electric effect increases proportionally to this intensity, because the *number* of electrons emitted increases in the same proportion. As long, however, as the frequency of the light is maintained constant, the velocity of the electrons is also constant. On the other hand, working with constant intensity of light but varying the quality or frequency it has been found that, on increasing the frequency of the light, the photo-electric effect increases, because the *speed* of the electrons is now increased. According to Lenard and Ladenburg, when the wave-length is thus shortened (at constant intensity), the velocity of the electrons emitted increases proportionally to the frequency. It is now known that the square of the speed is proportional to the frequency of the incident light. Below a certain wave-length or frequency, known as the threshold wave-length, the normal photo-electric effect is not observable. That is, with wave-lengths longer than a certain value λ_0—characteristic of the substance under examination—*no* electrons are emitted. Hughes has determined the value of λ_0 for a number of substances, using fresh surfaces, obtained by distillation of the substance *in vacuo*. These values are given in the following table:—

NORMAL PHOTO-ELECTRIC EFFECT. THRESHOLD WAVE-LENGTHS (λ_0).

Substance.	λ_0.	Substance.	λ_0.
Ca	370 $\mu\mu$	Sb	308 $\mu\mu$
Mg	330	As	236
Cd	314	Se	220
Zn	302	O_2	135
Pb	312	C (soot)	255-260
Bi	323		

The values obtained by Richardson and Compton with freshly scraped surfaces correspond to somewhat longer wave-lengths than those given.

Starting from the above threshold wave-lengths and diminishing the wave-length, the photo-electric effect increases in virtue of an increase in the velocity of the electrons. According to Richardson and Compton this goes on until a certain limiting value, corresponding to an extremely short wave-length is attained, beyond which the normal photo-electric effect no longer increases.

One of the most striking features of the photo-electric effect is the fact that the speed of the electrons is the same for a given quality (frequency) of light quite independent of the intensity of the light. Further, on keeping the intensity constant and varying the quality of the light, the speed of the electrons increases as the frequency increases. These two facts have found a satisfactory explanation on the basis of the quantum hypothesis, in which the light is regarded as "heterogeneous". The following statements indicate the view held by Sir J. J. Thomson in regard to the point under consideration (*Proc.*

Camb. Phil. Soc., **14**, 421, 1908): The [radiant] energy travelling outwards [from the radiating source] with the wave is not spread uniformly over the wave front, but is concentrated on those parts of the front where the pulses are travelling along the lines of force;[1] these parts correspond to the bright specks, the rest to the dark ground. . . . The energy of the wave is thus collected into isolated regions, these regions being the portions of the lines of force occupied by the pulses or wave motion. In fact, from this point of view, the distribution of energy is very like that contemplated on the old emission theory, according to which the energy was located on moving particles, sparsely disseminated throughout space. The energy is, as it were, done up into bundles, and the energy in any particular bundle does not change as the bundle travels along the line of force. Thus, when light falls upon a metal plate, if we increase the distance of the source of light, we shall diminish the number of these different bundles or units falling on a given area of the metal, but we shall not diminish the energy in the individual units; thus any effect which can be produced by a unit by itself, will, when the source of light is removed to a greater distance, take place less frequently it is true, but when it does take place it will be of the same character as when the intensity of the light was stronger. This is, I think, the explanation of the remarkable result discovered by Lenard, that though the number of corpuscles emitted by a piece of metal exposed to ultra-violet light increases [as intensity increases], the velocity with which individual corpuscles come from the metal does not depend upon the intensity of the light. If this result stood alone, we might suppose that it indicated that the forces which expel the corpuscles from the metal are not the electron forces in the light wave incident on the metal, but that the corpuscles are ejected by the explosion of some of the molecules of the metal which have been put into an unstable state by the incidence of the light; if this were the case the velocity of the corpuscle would be determined by the properties of the atom of the metal, and not by the intensity of the light, which merely acts as a trigger to start the explosion. Some experiments made quite recently by Dr. E. Ladenburg make, however, this last explanation exceedingly improbable. Ladenburg has investigated the velocities of corpuscles emitted under the action of ultra-violet light of different wave-lengths, and finds that the velocity varies continuously with the frequency; according to his interpretations of his experiments, the velocity is directly proportional to the frequency.[2] Thus, though the velocity of the corpuscles is independent of the intensity of the light, it varies in apparently quite a continuous way with the quality of the light; this would be very improbable if the corpuscles were expelled by an explosion of the molecule.

[1] Thomson assumes that the ether has disseminated through it discrete lines of electric force, these being in a state of tension. The light consists of transverse vibrations travelling along these lines.

[2] As already stated, the evidence now available goes to show that the square of the velocity of the electron is proportional to the frequency of the light.

It seems more reasonable to suppose that the velocity is imparted by the light, and yet, as we have seen, the velocity is independent of the intensity of the light. These results can, however, be reconciled by the view stated above, that a wave of light is not a continuous structure, but that its energy is concentrated in units (the places where the lines of force are disturbed), and that the energy in each of these units does not diminish as it travels along its line of force. Thus if a unit by impinging on a molecule can at any place make it liberate a corpuscle, it will do so and start the corpuscle with the same velocity whatever may be the distance from the source when it strikes the molecule; thus the velocity of the corpuscles would be independent of the intensity of the light. Ladenburg found that the velocity of the corpuscle increases with the frequency of the light; this shows that, if the view we are discussing is correct, the energy in the units will increase with the frequency of the light. This latter statement is, of course, in complete agreement with the quantum hypothesis, according to which the energy in any unit is directly proportional to the frequency, *i.e.* $\epsilon = h\nu$.

Einstein has given a quantitative application of the quantum hypothesis to the photo-electric effect in the expression—

$$Ve = \tfrac{1}{2}mv^2 = h\nu - h\nu_0.$$

The term $\frac{1}{2}mv^2$ is the kinetic energy of the electron emitted by light of frequency ν. ν_0 is the threshold frequency already defined, characteristic of the substance from which the electrons are emitted. The significance of Ve has already been pointed out. It follows from the above expression that when $\nu = \nu_0$ the electron will just not be emitted, ν_0 being therefore the lower limit of frequency capable of bringing about the photo-electric effect at all. Further, the frequency is proportional to the kinetic energy and therefore to the square of the velocity of the electron.

The applicability of the quantum theory to the photo-electric effect may be regarded as evidence of considerable value in favour of the quantum hypothesis itself—especially in the form given to it by Einstein.

Sir J. J. Thomson has likewise made an attempt to calculate the amount of energy in each unit of light of given frequency from some of Lenard's data. With the ultra-violet light used by Lenard the maximum velocity of the corpuscles was about 10^8 cms. per second; the kinetic energy ($\frac{1}{2}mv^2$) of a corpuscle moving with this speed is about 3×10^{-12} ergs. If we suppose that the energy of the corpuscle liberated is of the same magnitude as that of the light unit ϵ which liberated the corpuscle, we would expect ϵ (for the given light) to be about 10^{-12} ergs. It will be seen that this agrees very well with the values for ϵ already given as a result of calculation, with the help of Planck's constant h. A similar calculation, with equally satisfactory results, has been recently carried out by J. Franck and G. Hertz (*Verh. d. d. physik.*

Gesell., **13**, 967, 1911; *ibid.*, **14**, 167, 1012). The problem of the probable structure, constitution, and origin of these light units, as well as a criticism of Planck's views, has been considered by Sir J. J. Thomson (*Phil. Mag.*, 1908-10), but it would be quite outside the scope of this book to attempt anything further than this reference.

To show by an extreme case how *few* light units it is necessary to postulate, say, in the visible region of the spectrum under ordinary conditions, Sir J. J. Thomson has carried out the following calculation. Light of such intensity that 10^{-4} ergs fall on unit area per second would be very faint, but would still be visible. If we think of a cylinder of ether, base 1 square centimetre and 3×10^{10} cms. in length, then the above-mentioned intensity is such that 10^{-4} ergs are distributed throughout this cylinder (at any moment), and the density of the light is therefore $\frac{10^{-4}}{3 \times 10^{10}}$ ergs per c.c. Taking as a mean value for one quantun the number 10^{-12} ergs, we see that there will only be *one* such unit in every 1000 c.c. of space. The structure of light is therefore of a coarse-grained character. A further point still remains to be mentioned. The idea of a point source not radiating uniformly (this being a result of the heterogeneous nature of emission) seems to be in disagreement with the ordinary laws of propagation of light equally in all directions. It must be remembered, however, that any physical source of radiation consists of a very large number of resonators, so that the total radiating effect is on the average symmetrical about the source.

The phenomenon of ionisation of a gas or vapour by ultra-violet light is a further instance of the photo-electric effect. As is well known, ionisation of a gas may be brought about by means of cathode rays (*i.e.* streams of electrons) provided these electrons have attained a certain velocity, *i.e.* a kinetic energy $\frac{1}{2}mv^2$. In an electric discharge this velocity is reached as a rule before the electrons have travelled far, for they move with a positive acceleration towards the anode, the act of ionisation being demonstrated by a glow at some portion of the tube. This lower limit of kinetic energy which an electron must possess in order to ionise a gas may be equated to Ve, where V is called the ionisation potential of the gas, and denotes the smallest voltage which is required in order to give to an electron the kinetic energy $\frac{1}{2}mv^2$ which will just enable the electron to ionise a neutral gas molecule by impact. Applying the quantum theory to this case we see that the frequency ν_0 of the light which will just ionise a gas is given by $h\nu_0 = Ve$.

The following table contains the most recent values for the ionisation potential of a number of gases as determined by Hughes and Dixon (*Phys. Rev.*, **10**, 495 (1917)):—

Gas.	V in Volts.	Gas.	V in Volts.
H_2 . .	10·2	CO . .	7·2
O_2 . .	9·2	CO_2 . .	10·0
N_2 . .	7·7	NO . .	9·3
S . .	8·3 ?	CH_4 . .	9·5
Br_2 . .	10·0	C_2H_6 . .	10·0
Hg . .	10·2	C_2H_4 . .	9·9
HCl . .	9·5	C_2H_2 . .	9·9

Tate and Foote (*Journ. Wash. Acad. Sci.*, **7**, 517 (1917)) have determined the ionisation potential of sodium vapour to be 5·13 ± 0·10 volts; when ionised, the sodium vapour emits a brilliant yellow light. The theoretical value of the ionisation potential, using the wave-length limit of the principle series in the sodium spectrum, is 5·13 volts. These authors remark that this agreement affords another instance of the fundamental correctness of the theory of Bohr (*vide.* Chap. V.).

On referring to the results obtained by Hughes and Dixon, it will be observed that no general relation exists between the magnitude of the potential and the chemical nature of the substance or its stability. This is disappointing. It raises the question of what the actual significance of ionisation from the chemical standpoint really is. This point is further emphasised by certain results obtained by Richardson and Bazzoni (*Phil. Mag.*, **34**, 285 (1917)), which are briefly as follows :—

According to these authors, we may expect a limiting frequency in the spectrum of a substance, *i.e.* the spectrum comes to an abrupt end at a certain frequency or wave-length in the extreme ultra-violet region. Richardson and Bazzoni have determined this limit in the case of a few gases by allowing the radiation from the gas to strike a metallic target, thereby causing the emission of electrons whose velocities depend upon the frequency of the light. By employing a magnetic field it is possible to calculate the velocity of the fastest electrons, and hence by using the expression $\frac{1}{2}mv^2 = e\mathrm{V} = h\nu$ it is possible to calculate the limiting frequency ν emitted by the gas. In this way it was found that the limit of the helium spectrum occurs at 42 to 47$\mu\mu$. The hydrogen spectrum extends down to a limit somewhere between 83 and 95$\mu\mu$ (probably near 90$\mu\mu$), whilst in the case of mercury vapour the limit lies between 100 and 120$\mu\mu$. These limiting values correspond to certain ionisation potentials which can be calculated from the above relation. These potentials are decidedly higher than those found experimentally (*e.g.* the measurements of Hughes just cited), but these higher values appear to agree fairly well with the ionisation potentials calculated by Bohr (*cf.* Chap. V.). Thus Bohr calculated the ionisation potential of hydrogen to be 13 volts, whilst the potential corresponding to the above limiting frequency is 13·5 volts, a result decidedly higher than that found by direct experiment. According to Richardson the ionisation potentials

thus calculated bear no obvious relation to those obtained by Hughes and others.[1]

Let us return for a moment to the expression $h\nu_0 = Ve$. To test this expression we may take the case of oxygen. Hughes has found that the ionisation of air sets in at a wave-length $135\mu\mu$. This is likewise the position of the *absorption* band of oxygen in the ultra-violet. We may conclude, therefore, that the effect in air is due to the ionisation of oxygen, and hence we should be able to calculate the ionisation potential of oxygen from the expression $V = h\nu/e$. The value of V thus obtained is 9·2 volts which is identical with the observed value.

In dealing with collisions between electrons and molecules or atoms, it is necessary to distinguish between two *kinds*, namely, elastic collisions and inelastic collisions. In the first, the time of contact or encounter is very short compared with the second. No "chemical" effects are produced as a result of such collisions, the particles separating in the same chemical state and with the same momentum (though not, of course, with the same direction) as they possessed prior to the encounter. These are the kind of collisions postulated in kinetic molecular theory to account for the gas laws, for example. In the second kind of collision the time of encounter is longer, the total momentum after collision is less than it was before, and there is opportunity for transfer of energy between the two particles, which may result in observable chemical or physical change. This is consequently the more important kind from the standpoint of atomic interaction, ionisation, and resonance, etc. Tate and Foote (*Proc. Nat. Acad. Sci.*, **4**, 9 (1918)) point out that "no considerable transfer of energy from the light electron to the relatively heavy gas can take place except when the time of encounter between electron and atom *bears some simple relation* to the characteristic period of one of the vibrational degrees of freedom in the atom".

"Two *types* of *in*elastic encounter between electrons and gas atoms have been observed. One of these results in the emission of a radiation of a *single* frequency, *without ionisation of the gas*, whilst the other ionises the gas and causes it to emit *a composite spectrum* of radiations. The potential giving the first type of encounter may be termed a *resonance potential*, that giving the second type an *ionisation potential*. The line which defines the shortest wave limit or "convergence frequency" in the spectrum which is produced when the ionisation potential is applied, occurs much further in the ultra-violet than does the single line produced by the resonance potential. Naturally the single line characteristic of resonance also appears when the applied voltage causes ionisation. The following table is that given by Tate and Foote, and contains the values of resonance and ionisation potentials respectively. The calculated values of V in each case are obtained by employing the quantum expression $eV = h\nu$. Thus the conditions are chosen experimentally under which the gas emits only the single line. Its frequency

[1] These limiting wave-lengths appear, however, to lie fairly close to the *d spersional* wave-lengths. Accurate values for the dispersional wave-lengths have been obtained in a number of cases by Baly, *Phil. Mag.*, **27**, 632, 1914.

is determined and from the above expression the resonance potential is calculated. Again the conditions are obtained under which the gas is emitting a spectrum of lines, and from the shortest wave-length represented the ionisation potential is calculated by the aid of the formula. It will be seen that the values thus calculated agree extremely well with those observed. The observed values for the resonance and ionisation potential of mercury vapour are an addition to the table, and are due to Kunz (*Phys. Rev.*, **11**, 246, 1918).

RESONANCE AND IONISATION POTENTIALS.

Metal Vapour.	Resonance Potential. Observed.	Resonance Potential. Calculated.	λ in μμ.	Ionisation Potential. Observed.	Ionisation Potential. Calculated.	λ in μμ.
Cadmium .	3·88 volts	3·79 volts	326	8·92 volts	8·97 volts	137·9
Zinc . .	4·10 ,,	4·02 ,,	307·6	9·50 ,,	9·37 ,,	132
Potassium .	1·55 ,,	1·65 ,,	768·5	4·10 ,,	4·33 ,,	285·6
Sodium .	2·12 ,,	2·10 ,,	589·3	5·13 ,,	5·13 ,,	241·3
Mercury .	4·9 ,,			10·4 ,,		

It may be pointed out that the ionisation potential in the case of the above monatomic metallic vapours is approximately 2·3 times the resonance potential. No reason for this or any other relationship between the two has so far been suggested.

Whilst we are dealing with the question of *in*elastic collisions between electrons and atoms or molecules, it may be remarked that chemical effects produced, for example, in solutions are very probably due to the same kind of collisions. Thus the catalytic effect of hydrogen and other ions is probably due to the inelastic nature of the collision which permits of transfer of energy to the molecule catalysed. This appears to be borne out by the fact that in such cases there is a tendency for the formation of a compound between the two interacting individuals, and presumably compound formation is simply an extreme case of inelastic collision.

To return to the case of metallic vapours. The observations made in the case of mercury vapour are particularly interesting. From the resonance potential 4·9 volts it is easily calculated with the help of the quantum expression that the corresponding radiation has the wave-length 254μμ. Experiment has shown that this is actually the wave-length of the *single* line *emitted* by mercury vapour when the vapour is traversed by electrons whose velocities correspond to a potential of 4·9 volts. Further, there is a sharp band at the same position in the *absorption* spectrum of non-luminous mercury vapour (*cf.* McLennan and Edwards, *Phil. Mag.*, **30**, 695, 1915). Goucher (*Phys. Rev.*, **8**, 561, 1916) has found, as a matter of fact, three characteristic electron potentials in mercury vapour, *viz.* 4·9, 10·25, and 19 volts respectively. The first is evidently the resonance potential, the other two being apparently ionisation potentials. McLennan (*Proc. Roy. Soc.*, **A, 91**, 485, 1915)

had already suggested that more than one type of ionisation is to be expected. At the present time there is no general agreement as to the actual significance of each of these types.

We now turn to the *Selective Photo-Electric Effect.*

Elster and Geitel in 1894 discovered that in certain cases the photo-electric effect depended upon the plane of polarisation of the incident light. The substance examined by them was the liquid alloy of sodium and potassium. It was found that when light fell upon the surface at an angle of 45°, a *maximum* photo-electric current was produced when the electric vector of the light was vibrating in the plane of incidence. (Compare, however, the conclusions arrived at by Millikan, *infra.*) Further, in this so-called selective effect the number of electrons emitted has a maximum value for a particular frequency of the light. This maximum value occurs at a wave-length somewhat shorter than the threshold wave-length λ_0 (for the normal effect) and is not to be confused with λ_0 itself. For wave-lengths shorter than that corresponding to the maximum emission the selective effect rapidly falls off. The relative magnitude of the normal and selective effects are shown in the above diagram (Fig. 11).

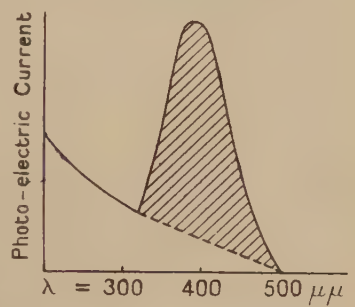

FIG. 11.—The dotted line indicates the normal effect; the maximum, the selective effect.

The position of the maximum in the selective effect occurs at the wave-lengths given in the following table (quoted from Hughes' *Photo-electricity*):—

Substance.	Maximum Selective Effect Occurs at
Rb	470-510 μμ
K	440
Na	340
Li	280
Ba	280

The same effect is observed when the metals are in the colloidal state in photo-electric cells. Thus the maximum sensitivity of such cells occurs at the following wave-lengths:—

Rb	480 μμ
K	440
Na	320
Cs	550

No general agreement has yet been arrived at regarding the relation of the selective to the normal effect. As indicating the obscure nature of the selective effect, it may be mentioned that Wiedmann (*Ber. d. Deutsch. phys. Gesell.*, **18**, 333 (1916)) has found that the presence of

hydrogen gas is essential to the production of the selective effect in the case of potassium. If the metal be repeatedly distilled *in vacuo* the selective effect is removed. It would be erroneous, however, to argue from this that the selective effect is accidental, due to some impurity. It is possible that in Wiedmann's case a temporary and unstable hydride is formed which, on decomposing, leaves the metal atom in a chemically activated state—differing as regards its electronic arrangement from the normal atom. Such chemical activation has been assumed in other connections. In the present connection all this is speculative however. According to Millikan and Souder (*Proc. Nat. Acad. Sci.*, **2**, 19 (1916)) there is an "essential identity" between the selective and photo-electric effects, evidenced by the following facts: the energy of emission is in all cases given by $\frac{1}{2}mv^2 = h\nu - p$, where p is the work necessary to separate an electron from the surface of the metal; the amount of emission is not dependent on the angle of incidence or on the azimuth of polarisation, but solely on the coincidence of the impressed frequency with the natural frequency; as an active gas acts progressively on a fresh surface the normal effect merges gradually into the selective.

As already pointed out in Chap. III., in connection with the fourth method of determining the characteristic infra-red frequency of a metal, Lindemann has suggested the following expression for the frequency ν_{violet} which corresponds to the position of the maximum of the selective photo-electric effect:—

$$\nu_{violet} = \frac{1}{2\pi}\sqrt{\frac{ne^2}{mr^3}}$$

where n is the valency of the atom to which the electron belongs, m the mass of an electron and r one half of the distance between two neighbouring atoms. It will be observed that r^3 is proportional to the atomic volume V of the metal. Hence the greater the atomic volume the smaller, *ceteris paribus*, the frequency. This is in agreement with the idea that a large atomic volume means that the electron is less firmly held and can therefore be set into movement by a quantum of relatively small magnitude, *i.e.* at a longer wave-length, than is the case with a substance of small atomic volume. The above expression can be put in a form which is convenient to use by first determining the value of the constant outside the square root by comparison with a single experimental determination. Thus Lindemann writes—

$$\nu_{violet} = 4{\cdot}594 \times 10^{15}\sqrt{\frac{n}{V}}, \text{ or } \lambda_{violet\ in\ \mu\mu} = 65{\cdot}3\sqrt{\frac{V}{n}}.$$

The following table indicates the degree of applicability of the formula:—

Element.	Atomic Volume.	Calculated λ.	Observed λ.
Cs . . .	70·6	550 μμ	550 μμ
Rb . . .	56·3	490	480
K . . .	45·0	438	440
Na . . .	23·5	317	320-340
Li . . .	11·9	225	280
Ba . . .	36·7	280	280
Sr . . .	34·5	271	—
Ca . . .	25·4	233	—
Mg . . .	14	172	—

Haber (*Verh. d. Deutsch. physik. Gesell.*, **13**, 1117, 1911) has given a very simple and interesting relation between the "ν_{violet}" and the Einstein infra-red characteristic frequency of the atoms of the same substance, which we may denote by "$\nu_{infra\text{-}red}$". This relation is—

$$\frac{\nu_{violet}}{\nu_{infra\text{-}red}} = \sqrt{\frac{M}{m}}$$

where M is the mass of the atom and m the mass of an electron. Haber has shown that this agrees extremely well with observed values. Thus, using Lindemann's formula just referred to to calculate ν_{violet}, one can make use of the Haber relation to calculate $\nu_{infra\text{-}red}$ and compare it with the values given by Lindemann's *melting-point* formula (for calculating $\nu_{infra\text{-}red}$). The results are as follows :—

Substance.	$\nu_{violet} \times 10^{-15}$.	$\nu_{infra\text{-}red} \times 10^{-12}$ Calculated by Haber.	$\nu_{infra\text{-}red} \times 10^{-12}$ Calculated by Lindemann's Melting-point Formula.
Li . .	1·27	11·26	10·78
Na . .	0·947	4·62	4·38
K . . .	0·685	2·55	2·57
Rb . .	0·612	1·55	1·56
Cs. . .	0·546	1·108	1·135
I . . .	0·905	1·87	1·85

A discussion of the above relation of Haber will be found in a paper by the writer (*Trans. Chem. Soc.*, **111**, 1086, 1917). The relation may be applied to compounds, but in some cases there is considerable doubt as to the significance of the term M. The relation is, in fact, semi-empirical.

Whilst we are dealing with the above relation, which demonstrates that there is a close connection between infra-red and ultra-violet characteristic vibration frequencies, it may be pointed out that Baly has recently discovered a relation between the position of the absorption band or bands in the ultra-violet spectra of certain substances and the frequency of the infra-red band exhibited by the same substances (compare Chap.

IV.). Baly has likewise shown the connection between absorption bands and fluorescence and phosphorescence bands. A summary of the latter work is given by Baly in the *Astrophys. Journ.*, July, 1915. Fluorescence is touched on briefly at the close of Chapter VII. For further information regarding the photo-electric effect, the reader is referred to Allen's *Photo-electricity* or to Hughes' *Photo-electricity*.

Photochemical Reactions. Einstein's Law of the Photochemical Equivalent.

In Chap. XIV. of Vol. II. we have already discussed photochemical reactions at some length. Our present purpose is to indicate briefly the mode of application of the quantum theory to photochemical change.

At the present time there appears to be a somewhat general tendency to regard photochemical reactions as primarily due to a photo-electric effect.[1]

As the photo-electric effect is itself independent of temperature, the whole process is only slightly affected by temperature, *i.e.* photochemical reaction velocity constants have very small temperature coefficients.

The most important application of the quantum theory to photochemical processes is that of Einstein as expressed in his *law of the photochemical equivalent.*

(A. Einstein, *Ann. d. Physik*, [4] **37**, 832, 1912.)

According to Einstein, a photochemical reaction takes place owing to the absorption of radiation in terms of *quanta, each single molecule of a photo-sensitive substance requiring just one quantum* $h\nu_0$ (*of the requisite frequency* ν_0 *which the substance itself can absorb*) *in order that it may be decomposed.* So far as experiment has gone, the law has been approximately verified. Bodenstein (*Zeitsch. Physik. Chem.*, **85**, 329, 1913) gives a table of several reactions from which it will be seen that if not a single quantum, at least a very small number, 2 to 5, are required per molecule of the substance photochemically decomposed. Such discrepancy as does exist is probably to be attributed to the fact that the experimental conditions did not correspond closely enough to those postulated by Einstein, the principal one of which is that there shall be the same intensity or density of radiation throughout the system. If the system absorbs light very strongly, and is only illuminated in one direction, this condition will not be fulfilled, and instead of reaching a true equilibrium governed, as Einstein supposes, by an expression analogous

[1] In this connection, compare Landsberg (*Journ. Russ. Phys. Chem. Soc.*, **47**, 908 (1915)); Nazarov, *ibid.*, p. 943; (*Chem. Soc. Abstracts*, **108**, ii., 718, 754 (1915)). Volmer (*Zeitschr. Elektrochem.*, **21**, 113 (1915)) concludes that the close relation between photo-electric conductivity and photochemical sensitiveness "confirms the Luther theory that a loosening of electrons is the immediate cause of photochemical processes".

to the ordinary mass action law, we shall meet with photochemical stationary states instead, such as those realised in the anthracene-dianthracene reaction.

Einstein's general argument is as follows. Consider a gas mixture containing three different species, whose molecular weights are m_1, m_2, and m_3, and suppose there are n_1, n_2, and n_3 gram-molecules of each of these present, the reaction considered is one in which 1 molecule of m_1 decomposes photochemically into 1 molecule each of m_2 and m_3, an equilibrium point finally being reached. The first assumption made is that the decomposition of m_1 proceeds (owing to the absorption of radiation) independently of the presence of the other species. The second assumption is that the probability that an m_1 molecule decomposes in a given time is proportional to the density ρ of a given monochromatic radiation to which the system is exposed. From these two assumptions it follows that the number Z of m_1 molecules decomposing per unit time can be written—

$$Z = A\rho n_1$$

where A is a proportionality factor which depends only upon the temperature T of the gas mixture.

As regards the recombination process, Einstein assumes it to be an ordinary bimolecular reaction (which emits[1] the radiation first absorbed by the m_1 molecules). If Z_1 denotes the number of m_1 molecules thus re-formed per unit of time, we can write—

$$Z_1 = A' \cdot V \cdot \frac{n_2}{V} \cdot \frac{n_3}{V}$$

where V is the volume of the system ($\frac{n_2}{V}$ and $\frac{n_3}{V}$ denoting the concentrations of each of these species). A′ likewise only depends upon the temperature T of the gas, not upon ρ (assumption 3), and if the temperature be kept constant, A and A′ are constant. When thermodynamic equilibrium is reached, *i.e.* equilibrium between the matter involved and the radiation itself, we can equate the two quantities, supposing Z and Z_1 to refer to this case. That is, we obtain the relation—

$$\frac{\frac{n_2}{V} \cdot \frac{n_3}{V}}{\frac{n_1}{V}} = \frac{A}{A'\rho}.$$

Einstein now proceeds to consider a small virtual change of the

[1] The object of making this assumption is to maintain the radiation equilibrium. A more detailed examination of the mechanism of chemical change, discussed in the concluding section of the present chapter and also in Chap. VII., leads to the conclusion that the act of decomposition *or* of union involves first of all an absorption of energy followed by an evolution. The radiation equilibrium is, nevertheless, maintained when mass action equilibrium has been reached owing to the equality of the absorption and evolution effects in the system as a whole.

system which is accompanied by a small change in the entropy of the matter and in the entropy of the radiation, finally obtaining as a criterion of the above equilibrium state, the relation—

$$\rho = \frac{A'a}{A} \cdot e^{-N\epsilon/RT_s}$$

where a stands for a complex expression, involving the temperature T of the gas (which is independent of the temperature T_s of the radiation), ϵ is the quantity of energy absorbed per molecule of substance m_1, the energy being in the form of monochromatic radiation ν_0, the density of the radiation being ρ, and N the number of molecules in 1 gram-molecule. "Since T_s and ρ are independent of the gas temperature T, the magnitudes $\frac{A'a}{A}$ and ϵ must also be independent of T. Since these quantities are also independent of T_s, we arrive at the same relation between ρ and T_s as is expressed in Wien's radiation formula." Since Wien's formula only holds for the short wave region, Einstein's relation in the first instance is likewise restricted to this region. "If we write Wien's radiation formula after introducing the Planck constants h and k, we obtain—

$$\rho = \frac{8\pi h\nu^3}{c^3} e^{-h\nu/kT_s}$$

and on comparing this with the previous equation, we see that—

$$\epsilon = h\nu_0$$

and

$$\frac{A'a}{A} = \frac{8\pi h\nu_0{}^3}{c^3}.$$

The most important consequence of the above is that $\epsilon = h\nu_0$, which shows that one gas molecule which decomposes under radiation of frequency ν_0 absorbs in its decomposition just $h\nu_0$ of energy, *i.e.* 1 quantum, as a mean value.

Bodenstein (*loc. cit.*) has collected the results of a number of investigations carried out by various authors, with the object of showing how far the law of the photochemical equivalent is borne out by experiment. That it is so at least approximately is shown by the following table:—

Reaction Studied.	Number of $h\nu$ Required to "Decompose" one Molecule.
$3O_2 = 2O_3$	1 for $2O_3$ formed
$2NH_3 = N_2 + 3H_2$	4
2 anthracene → 1 dianthracene	0·7 to 3
$S_\lambda = S_\mu$	4 to 5
Oxidation of quinine by chromic acid	1·5
$2O_3 = 3O_2$ (effected by means of chlorine)	0·8 to 1·7
Nitro-benzaldehyde into nitro-benzoic acid	9

Bodenstein gives other instances in which the law appears to break down badly, one quantum decomposing many molecules. Even in the cases quoted the results are subject to considerable uncertainty. One of the principal reasons for this is, in the writer's opinion, the fact that the wave-length of the light employed did not correspond sufficiently closely to the head of the absorption band of the substance decomposing. Einstein assumes that the decomposition is brought about by a single definite frequency. As is well known, absorption bands exhibit width, especially when the concentration of the substance is fairly large, and, further, experiment goes to show that any wave-length inside the band is capable of bringing about the photochemical effect. It is not to be expected, however, that all wave-lengths inside a band will be equally efficient. To test the Einstein expression in the most unequivocal manner it would appear to be necessary to select the wave-length which corresponds to the head of the band. In the case of other wave-lengths, still inside the band, it is probable that a considerable fraction of the radiation absorbed is not converted into chemical change, but is simply degraded into quanta of smaller size, *i.e.* degradation into heat. This indeed appears to be the case in a number of experiments of Warburg (*Sitzungsber. kön. preuss. Akad.*, 1912-15) on the ozonisation process, in which the wave-length employed ($209\mu\mu$) does not correspond to the position of maximum absorption of oxygen. The fact that an absorption band exhibits width, and further, the fact that the width increases with the concentration of the material is probably due to collisions which set up forced vibrations inside the molecule thereby disturbing the normal electronic period or frequency which an isolated molecule would possess.

In the case of photochemical reactions in solution, effects due to the solvent may be anticipated. This important problem has been dealt with by Baly (*Physikal. Zeitsch.*, **14**, 893 (1913)) in the following manner:—

According to Baly, the chemical reactivity of an atom or molecule is due to the existence of atomic electro-magnetic fields of force, which differ from atom to atom in the density and location of the lines of force. When an atomic or molecular species is activated in the chemical sense, this is due to an "opening up of the atomic fields of force" which are thus capable of interacting with the corresponding fields of other atoms, thereby producing chemical change. This "opening up" can be brought about essentially by two agencies, (1) by the absorption of light, and (2) by the solvent (which presumably acts in an analogous manner in virtue of its electro-magnetic properties). Different solvents are capable of "opening" the field of a molecule to different extents, these different extents or stages being manifested by the different positions of the absorption band or bands possessed by the dissolved substance in various solvents. On this basis we would expect that a substance dissolved in a given solvent, being already partially activated, would require less energy, say of the radiational type, to complete the activation, than the same substance would require in the absence of the

solvent. Baly's argument is, therefore, that in the case of a dissolved substance reacting photochemically, less energy is required per molecule than is required for the same substance in the gaseous state; and hence Einstein's law does not apply quantitatively in such a case. In other words, one quantum can apparently activate numerous molecules. Baly suggests that this affords an explanation of the results obtained by Henri and Würmser (*Journ. de Physique*, [5], **3**, 305 (1913)) in connection with the decomposition of hydrogen peroxide and of acetone in aqueous solution. In both of these cases the amount of energy actually required is considerably less than that demanded by Einstein's law, in fact, only 1 to 0·1 per cent. of the "theoretical" value. As Henri and Würmser point out, the light in these cases acts as a catalyst, accelerating but not initiating the reaction. Baly's view, which gives the possible mechanism of such photo-catalysis, is further borne out by the statement of Henri and Würmser that the above reactions will occur in the dark, *i.e.* the solvent itself is evidently capable of bringing them about. On the other hand, it is precisely in those cases in which solvent is absent that we find the closest approximation to Einstein's law. At the present time we do not possess as satisfactory experimental evidence for Einstein's law as we could wish, but the law may be regarded as substantiated at least approximately.

Einstein's law depends upon Wien's radiation expression. It is therefore restricted to regions in which the wave-length is not very long. It will be shown in the next section that it is justifiable to regard Einstein's law as applicable down to the short infra-red region, *i.e.* the region which is responsible for so-called thermal reactions at ordinary temperatures.

Thermal Reactions. Reaction Velocity from the Standpoint of the Quantum Theory.

By the term thermal reactions is meant reactions of the "ordinary" kind which proceed without being exposed to any definite external source of short-wave radiation such as we meet with in the so-called photochemical reactions. The fundamental difference between the two kinds of reaction is, as we shall see, the fact that in photochemical reactions, as ordinarily carried out, the temperature of the active radiation is very much higher than the temperature of the material system affected, whilst in the case of thermal reactions, the temperature of the effective radiation is identical with that of the material system itself.

Photochemical phenomena have demonstrated the fact that chemical change can be brought about as a result of absorption of radiation in the short-wave region. We are led to generalise this and to seek in radiation of longer wave-length the ultimate cause of ordinary or thermal reactions as well. It is obvious that every material system, in virtue of its temperature, contains radiation at the same

tempearture. Under ordinary conditions, *i.e.* at ordinary temperatures, this radiation is mainly of the infra-red type. It is well known that electro-magnetic properties of substances, *e.g.* the dielectric constant, are intimately connected with the radiation density in the material, and further, such properties have a marked effect upon the chemical reactivity of molecules, *e.g.* the electrolytic dissociating power of solvents which possess high dielectric constants. It will be readily accepted, therefore, that infra-red radiation is the source of the energy which is required to bring about ordinary or thermal reactions. The problem before us is to discover how this concept may be applied in as quantitative a manner as possible. An attempt in this direction, made by the writer (*inter alia*, *Trans. Chem. Soc.*, **109**, 796 (1916)), will be considered briefly here.

For our present purpose, the most significant phenomenon associated with thermal reactions is the influence of temperature upon the reaction velocity, the velocity constant increasing three or four fold for a rise of 10° in the neighbourhood of room temperature. It has long been known that this very great effect cannot be accounted for simply on the basis of an increase in the kinetic energy of translation of the molecule as a whole, for in the most favourable case, this increase could not account for more than 1 or 2 per cent. of the observed effect, and it is doubtful whether the change so produced would be even in the right direction. It is evident, therefore, that the effect of temperature upon the velocity constant has to do not with the kinetic energy of translation but with the internal energy of the molecule.[1]

By treating the problem of reaction velocity from the point of view of statistical mechanics it is possible to correlate the velocity constant with the temperature, as has been done by Marcelin, and later in a more exact manner by J. Rice (*Brit. Ass. Rep.*, 1915, p. 397). The relation between the observed velocity constant k and the absolute temperature T for a simple type of gaseous reaction is shown by Rice to be—

$$d \log k/d\mathrm{T} = \mathrm{E}/\mathrm{RT}^2.$$

This expression is, as a matter of fact, a slightly simplified form, a small term having been neglected. In deducing this expression it has been assumed that a molecule reacts when its internal energy has been raised to a certain critical value which is in general large compared with

[1] From measurements of specific heat it is known that, *on the average*, the increase in internal energy per degree rise in temperature is not large. In the simplest cases the increase in internal energy varies directly as the absolute temperature, and hence a rise of 10° would cause an increase of approximately 3 per cent. in the average internal energy at ordinary temperatures. The influence of temperature on velocity cannot be ascribed therefore to the average increase in internal energy. When heat is added to a body, however, the energy does not distribute itself evenly among the molecules; instead, some receive no energy, others a moderate amount, and a very few receive excessively great amounts of energy. It would seem therefore that the influence of temperature on reaction-speed is to be sought in the fact that a very small number of molecules receive an abnormally large quantity of internal energy.

the average internal energy of the molecule. This critical limit is known as the critical energy of the molecule. The term E denotes the difference between the critical energy and the average or mean internal energy reckoned per gram-molecule. E may therefore be called the critical increment; E denotes the amount of energy which has to be added to make an average [gram]-molecule react. It is at this point that the radiation hypothesis of chemical reactivity enters, the assumption being that the quantity E is contributed by the absorption of infra-red radiation of a given frequency which the substance is capable of absorbing. It is assumed that this energy is communicated in terms of quanta, the same assumption as is made by Einstein in obtaining his expression for the photochemical equivalent.

It will be observed that the Marcelin-Rice equation is identical in form with the empirical equation of Arrhenius, already discussed in Vol. I., which is known to be in good agreement with experiment. A considerable advance has been made, however, in that the empirical term A which occurs in Arrhenius' equation is now replaced by the term E to which a definite physical significance can be attached. In the case of polymolecular reactions the active molecular state actually exists, as is shown by the experiments of Baly and F. O. Rice (*Trans. Chem. Soc.*, **101**, 1475, 1912); the rate of observed chemical reaction depends then upon the frequency of collision between activated molecules.

In the case of unimolecular change molecules in the active state do not exist, for it is assumed that when a molecule becomes active it immediately decomposes and becomes transformed into resultant. If the reaction be reversible it follows, on the statistical basis of the expression, that the *activated* resultant has exactly the same critical *energy* as the activated reactant. This does not mean that the E term is the same for both reactant and resultant, E being the difference between the critical and mean internal energies.[1]

Having indicated in a general way the rôle which radiation plays in regard to the activation of a molecule, it is now necessary to show how an expression analogous to that of Marcelin and J. Rice may be obtained on the basis of Planck's radiation theory.

In order that any of Planck's relations may be applied it is essential that temperature radiation alone be considered, and further, that the radiation and the matter composing the system be in temperature equilibrium. On Planck's view, the interchange between matter and radiation is effected through the medium of oscillators, situated on the molecules of the substances composing the system. In the case of thermal reactions occurring at constant temperature in a thermostat (which defines the temperature of the system both with regard to the

[1] Granted that the critical increment is due to radiation, and further assuming that a single quantum is capable of accounting for the E of a single molecule, it can be easily shown from a knowledge of the magnitude of the temperature coefficient of a reaction, that the effective radiation must belong to the short infra-red region, *i.e.* of the order 1 to 3μ, in the case of reactions which occur with sensible velocity at ordinary temperatures.

radiation and to the material), Planck's theory may be applied with some degree of certainty. In this connection the following statement made by Planck (*Theory of Heat Radiation*, Eng. ed., p. 7) is of importance: "A special case of temperature radiation is the case of the chemical nature of the emitting substance being invariable. Nevertheless, it is possible, according to what has been said, to have temperature radiation while chemical changes are taking place, provided the chemical condition is completely determined by the temperature."

Conditions for Reactivity on the Radiation Hypothesis.

According to the law of mass action the reactivity of a substance is measured by its active mass. Since the time of Guldberg and Waage it has been considered sufficient to regard the concentration of the substance as an accurate measure of the active mass, and this has been borne out by an accumulation of experimental results, which serve to demonstrate the general truth of the hypothesis. At the same time numerous facts are known which indicate that concentration *per se* is not the only factor determining reactivity. To attempt to extend the principle of mass action so as to allow for environment, it is necessary to take into account the energy exchanges which accompany, or rather precede, molecular change, for as the fact of a *finite* velocity demonstrates, all the molecules of a system are not at any one moment in the same reactive state. From what has already been said regarding the absorption of energy by an average molecule to bring its energy content to the critical value, it will be evident that the amount and nature of the radiation present in the system must play a definite part in the reactivity of a given species. From this point of view, therefore, the active mass of a species is not simply proportional to its concentration, but is simultaneously dependent on the radiational environment, the observed reactivity being due to the product of these two effects. The active mass is, in the case of unimolecular decomposition, identical with the number of molecules brought per second into the active state by means of the radiation present in the system. The fundamental assumption is that the radiational environment can be identified with the radiation density of the absorbable type present throughout the system. That is, the active mass of a species, spontaneously decomposing, is proportional to its concentration, multiplied by the radiation density of the type which the substance can absorb, the radiation being present in virtue of the temperature of the system. The radiation density, u_ν,[1] is the amount of radiation made up of quanta corresponding with a certain frequency ν, which is present in unit volume of the system, when the radiation and the matter are in thermal equilibrium. If the radiation density is too small the substance will not react, however great its concentration may be. On this view the function of the

[1] As already pointed out u_ν has not the dimensions of energy density; the actual expression for energy density is $u_\nu d\nu$. The term u_ν may be called the radiation density *factor*.

solvent acting as a positive catalyst is to increase the radiation density of the type absorbable by the reactant, whereby a greater number of the molecules of the reactant attain the critical value for their internal energy per second, with the result that the reaction-velocity is increased.

Planck's expression for the radiation density factor may be written in the following form :—

$$u_\nu = \text{constant} \times \frac{1}{e^{h\nu/kT} - 1}$$

where h is Planck's constant, k the gas constant per molecule, and T the absolute temperature. For the short infra-red region the above expression reduces to the following one,[1] which is identical with the expression of Wien :—

$$u_\nu = \text{constant}\, e^{-h\nu/kT}.$$

This expression may be regarded as holding for a gaseous system. To simplify the treatment still further we shall assume that the reaction considered is unimolecular, and that a single frequency is absorbed by the substance in the process of activation. For this case the rate of reaction can be written in the following way, in which a denotes as usual the initial concentration of the substance and x is the amount transformed after a time t: dx/dt is proportional to $(a - x)u_\nu$, or

$$dx/dt = \text{constant}\, (a - x)e^{-h\nu/kT} \quad . \quad . \quad . \quad (1)$$

On integrating this expression we obtain—

$$\frac{1}{t} \log \frac{a}{a - x} = \text{constant} \,.\, e^{-h\nu/kT} \quad . \quad . \quad . \quad (2)$$

At constant temperature this expression becomes identical with the ordinary mass action expression. Further $\frac{1}{t} \log \frac{a}{a - x} = k_{obs}$, where k_{obs} is the experimentally determined velocity constant. Hence—

$$k_{obs} = \text{constant} \times e^{-h\nu/kT} \quad . \quad . \quad . \quad . \quad (3)$$

The "constant" which occurs here is practically independent of temperature, especially for a gaseous system. We can find the effect of temperature upon the observed velocity constant by simply differentiating the above expression with respect to T. The resulting expression is—

$$d \log k_{obs}/d\mathrm{T} = h\nu/k\mathrm{T}^2 \quad . \quad . \quad . \quad . \quad (4)$$

But k, the gas constant per molecule, can be written as R/N where R is the gas constant per gram-molecule and N is the number of molecules in one gram-molecule. Hence—

$$d \log k_{obs}/d\mathrm{T} = \mathrm{N}h\nu/\mathrm{RT}^2 \quad . \quad . \quad . \quad (5)$$

[1] *Cf.* W. C. M. Lewis, *Brit. Assoc. Report*, p. 394, 1915.

The term $N\hbar\nu$ is a constant, characteristic of a given substance, and independent of the temperature. It may therefore be denoted by the symbol A, whence we obtain—

$$d \log k_{obs}/dT = A/RT^2 \quad . \quad . \quad . \quad . \quad (6)$$

This expression is identical in form with the empirical relation of Arrhenius which is known to be in agreement with experiment for a great variety of reactions. The fact that this relation can be deduced on the basis of the radiation hypothesis of chemical reactivity constitutes strong evidence in favour of the hypothesis itself.

Let us now compare equation (5) with that obtained by Marcelin and J. Rice, namely—

$$d \log k/dT = E/RT^2.$$

On equating like terms it follows that—

$$E/N = h\nu.$$

But E/N represents the amount of energy which has to be added to a *single* molecule to make it react, and by the above relation this is just one quantum of the absorbable radiation. This is simply a statement of the Einstein law of the photochemical equivalent, which is now shown to be applicable to ordinary or thermal reactions caused by radiation of the short infra-red type. That this result is to be expected follows from the fact that for radiation of this type Planck's expression reduces to that of Wien, upon which Einstein founded his law.

The radiation hypothesis has been extended to solute catalysis. It is not proposed to enter into this question in the present instance except to point out that the following general conclusion is arrived at: the presence of a positive catalyst diminishes the temperature coefficient, *i.e.* decreases E, whilst a negative catalyst increases the temperature coefficient.

CHAPTER VII.

(Systems in chemical equilibrium)—Relation between Nernst's heat theorem and the quantum theory—Mass action equilibrium and heat of reaction in terms of the quantum theory.

Nernst's Heat Theorem and the Quantum Theory.

We have already seen (Chap. III.) that the quantum theory applied to atomic heat of solids leads us to expect that at very low temperatures the atomic heat will become practically zero. If we think of two solids A and B we can state that at low temperatures—

$$dU_A/dT = dU_B/dT = 0$$

or

$$d(U_A - U_B)/dT = 0.$$

If the solid substances A and B are the reactant and resultant respectively of a chemical reaction, the expression $(U_A - U_B)$ represents the change in internal energy, U accompanying the reaction. Hence the quantum theory leads to the conclusion that in a chemical reaction between solids at very low temperatures—

$$dU/dT = 0.$$

This, as far as it goes, is in complete agreement with Nernst's heat theorem which states (*cf.* Chap. XIII., Vol. II.) that—

$$\text{limit, } T = 0 \begin{cases} dA/dT = 0 \\ dU/dT = 0. \end{cases}$$

To show that the relation $dA/dT = 0$ is likewise in agreement with the Planck-Einstein hypothesis regarding the energy distribution in solids, we may proceed as follows: As the molecules or atoms of a solid at very low temperatures do not possess any sensible kinetic energy of vibration, their mutual distance apart will change very little with temperature over a limited range in this region. Consequently, the mutual potential energy of the atoms or molecules will remain practically unchanged, and hence their free or available energy, which depends upon the potential energy, will also remain unchanged. That is, in the limit, when $T = 0$, $dA/dT = 0$. The same conclusion may be arrived at in a slightly different way. We know that the intensity of radiation, and therefore the amplitude of the resonators (*i.e.* the atoms), increases with the temperature according to a power law considerably greater than the first. Hence, as temperature falls the amplitude will decrease much more rapidly, finally becoming exceedingly small. Again, the potential

energy, and therefore the free energy, may be regarded as sensibly independent of the temperature when the temperature is low. It cannot be said, of course, that the validity of the Planck-Einstein theory is a proof of the validity of Nernst's heat theorem. They are, however, in agreement. This point will perhaps be rendered clearer by the following considerations.

We know that in the case of any process carried out reversibly, the Gibbs-Helmholtz equation states—

$$A - U = T \cdot (dA/dT)_v.$$

Further, $A - U = Q$ where Q is heat absorbed in the process.

Hence $Q/T = S = (dA/dT)_v$, where S is the change in entropy of the system as a result of the process. Applying Nernst's theorem we conclude that at very low temperatures the change in entropy due to the process is zero. In other words, Nernst's theorem is identical with the statement that at absolute zero the entropy of all substances is the same. Planck has already pointed out (*cf.* Chap. I.) that the quantum hypothesis is equivalent to the assumption that the entropy of all substances at absolute zero is zero also. This is really a special case of the conclusion involved in Nernst's heat theorem. The theorem and the quantum theory are therefore in agreement, but the heat theorem is independent of the quantum hypothesis.[1]

Calculation of the Affinity of a Chemical Process from Thermal Data by the Simultaneous Application of Nernst's Heat Theorem and the Quantum Theory of Atomic Heats.

Equations (3) and (4) of Chap. XIII. of Vol. II., which express the Nernst heat theorem, contain certain coefficients β, γ, etc., which are calculated from measurements of the molecular or atomic heats of the reactants and resultants of the reaction considered. These terms are, in fact, the temperature coefficients of the molecular heats of the reacting substances. In principle, the introduction of the quantum theory (say in the form of the Nernst-Lindemann equation) is simply a matter of substitution of this equation in the original equations of Nernst for A and U. To indicate how this is carried out in practice it is necessary to put the Nernst equations into a more general form than that expressed by the equations (3) and (4) referred to.

The change, U, in the internal energy of a system as a result of a chemical reaction is, by definition, the difference of the internal energies of reactants and resultants, reckoned in terms of the stoicheiometrical quantities required for the reaction. For any single substance Z we can write: $dU_z/dT = c_z$, where c_z denotes the molecular heat of the substance Z at constant volume. Hence $U_z = \text{constant} + \int_0^T c_z dT$. Hence

[1] The relation between the heat theorem and the quantum theory is further considered by O. Sackur (*Annalen der Physik*, 34, 455, 1911).

for the quantity U, which involves the algebraic sum of a number of such terms, we can write—

$$U = U_0 + \int_0^T \Sigma nc\,dT$$

where U_0 is the change in internal energy accompanying the reaction at absolute zero, and n denotes the number of moles of reactants and resultants (with proper sign) which take part in the reaction.

We have now to express the molecular or atomic heat c of each reacting substance in terms of the Nernst-Lindemann equation. Having done this we find that the above integral may be evaluated thus—

$$\int_0^T \Sigma nc\,dT = 3R\Sigma\left(\frac{\beta_0\nu}{e^{\beta_0\nu/T} - 1} + \frac{\beta_0\nu/2}{e^{\beta_0\nu/2T} - 1}\right).$$

Hence—

$$U = U_o + \frac{3}{2} R\Sigma\left(\frac{\beta_0\nu}{e^{\beta_0\nu/T} - 1} + \frac{\beta_0\nu/2}{e^{\beta_0\nu/2T} - 1}\right) + \frac{3}{5}\Sigma aT^{5/2} \quad . \quad (1)$$

The final term is an empirical correction, which has to be added to allow for the fact that the experimental measurements of molecular or atomic heats refer to constant pressure, whilst the quantities to which the Nernst-Lindemann expression refer are molecular or atomic heats at constant volume. (*Cf.* Magnus and Lindemann (*Zeitsch. Elektrochem.*, **16**, 369 (1910)); a more exact correction is given by Nernst and Lindemann (*Zeitsch. Elektrochem.*, **17**, 817 (1911)).)

We have now to consider the free energy term A. On the basis of the first and second laws of thermodynamics we have already seen that—

$$\frac{A}{T} = a - \int_0^T \frac{U}{T^2} \cdot dT.$$

Further, Nernst's theorem leads to the conclusion that $a = o$, and therefore we can write—

$$A = -T\int_0^T \frac{U}{T^2} \cdot aT.$$

Again writing—

$$U = U_0 + \int_0^T \Sigma n_c dT,$$

and substituting this in the above integral, and also substituting the Nernst-Lindemann expression, we obtain—

$$A = U_0 - \frac{3}{2} R\Sigma\left[\frac{3}{2}(\beta_0\nu) - \log_e(e^{\beta_0\nu/T} - 1) - \log_e(e^{\beta_0\nu/2T} - 1)\right]$$

$$- \frac{4}{15}\Sigma aT^{5/2} \quad . \quad . \quad . \quad . \quad (2)$$

Equations (1) and (2) express the Nernst heat theorem in terms of the quantum theory.

[NOTE.—The mode of obtaining equations (1) and (2) is given in detail in Pollitzer's article, *Die Berechnung chemischer Affinitäten nach dem Nernstchen Theorem*, Ahrens Sammlung, **17**, 1912. To facilitate calculation Pollitzer has included as an appendix a number of tables giving the Einstein and Nernst-Lindemann functions for various values of β_0 and ν.]

We now proceed to consider an actual case, namely, the affinity of silver for iodine investigated by U. Fischer (*Zeitsch. Elektrochem.*, **18**, 283, 1912). The treatment of a number of difficulties met with is instructive and is therefore given in some detail.

The first question taken up by Fischer is the *heat of the reaction*—

$$\underset{\text{(solid)}}{2Ag} + \underset{\text{(solid)}}{I_2} = \underset{\text{(solid)}}{2AgI}$$

The direct measurements of Thomsen and of Berthelot being unsatisfactory, recourse was had to the Gibbs-Helmholtz equation—

$$A' - U = T\frac{\partial A'}{\partial T}$$

or

$$E - U = T\frac{\partial E}{\partial T}$$

as applied to the measurement of the e.m.f. of the cell—

$$Ag \mid KI \text{ solution, saturated with } AgI \mid I_2$$

at several temperatures.

The results were as follows :—

Employing $\frac{N}{2}$ KI solution, $E_{volts} = 0{\cdot}6948 + 0{\cdot}000305t$

" $\frac{N}{3}$ " $E_{volts} = 0{\cdot}6932 + 0{\cdot}000305t$

" $\frac{N}{10}$ " $E_{volts} = 0{\cdot}6916 + 0{\cdot}000305t$

the temperature t being given in degrees centigrade.

These values for the e.m.f. require a correction, however, owing to the fact that some of the iodine from the right-hand electrode dissolves in KI, giving tri-iodide (and other polyiodides, the quantity of which may, however, be neglected). This causes the concentration of the iodine ion I′ on the iodine side of the cell to be diminished, and the concentration difference of I′ on the two sides of the cell give rise to an e.m.f. e, where—

$$e = RT \log_e \frac{c_1}{c_2}$$

$\frac{c_1}{c_2}$ being the ratio of the I′ ion concentrations. With the help of the data of von Ohlendorff, and some experiments of his own on the solu-

bility of iodine in potassium iodide, Fischer succeeded in calculating the value of e for the three cases considered, *viz.* $\frac{N}{2}$, $\frac{N}{3}$, and $\frac{N}{10}$KI respectively. The following table contains the corrected value of the e.m.f. and the temperature coefficient $\frac{dE}{dT}$:—

KI Solution.	Temperature, °C.	e.	E Corrected.	$\frac{dE}{dT}$.
$\frac{N}{2}$	13·1	0·01708	0·6817	2·419
	23·8	0·01869	0·6833	
	35·3	0·02154	0·6839	
$\frac{N}{3}$	14·9	0·01719	0·6805	1·267
	24·6	0·01938	0·6813	
	38·6	0·02327	0·6817	
$\frac{N}{10}$	13·1	0·01658	0·6791	1·66
	23·9	0·01848	0·6805	
	35·4	0·02118	0·6807	

Employing these data in the Gibbs-Helmholtz equation, Fischer found for 15° C. (288° abs.):—

$\frac{N}{2}$KI solution, $U = 0{\cdot}6821 \times 23046 - 288 \times 2{\cdot}419$

$= 15{,}023$ cals.

$\frac{N}{3}$KI „ $U = 0{\cdot}6806 \times 23046 - 288 \times 1{\cdot}267$

$= 15{,}315$ cals.

$\frac{N}{10}$KI „ $U = 0{\cdot}6791 \times 23046 - 288 \times 1{\cdot}66$

$= 15{,}216$ cals.

The mean value of U is 15,169 cals.

Besides this indirect method of measuring U, Fischer also employed a calorimetric method, precipitation of insoluble salt being avoided by the following very ingenious procedure due to von Wartenberg. As solvent a 3N,KCN solution was employed, and in this was placed a known weight of silver powder. The silver is not attacked by the KCN. To the liquid was added a known weight of iodine, the following reaction taking place:—

$$Ag + I + 2KCN = AgK(CN)_2 + KI \quad . \quad . \quad (1)$$

The heat effect of this reaction was measured. Then using a similar solution of KCN, a known weight of silver iodide was added (no silver powder being present in this case), the resulting reaction being—

$$AgI + 2KCN = AgK(CN)_2 + KI \quad . \quad . \quad . \quad (2)$$

The difference of the heat effects of the reactions (1) and (2) gives the heat effect desired, *viz.*—

$$Ag + I \rightarrow AgI.$$

The mean value thus obtained was U = 14,280 cals., which agrees pretty closely with the result of the first method. Fischer made use of still another calorimeter method, in which some of Thomsen's data on other salts were employed, the results being less trustworthy. [Note that this is a heat effect at constant volume, since the system does not alter appreciably in volume.]

Now, if we consider the cell—

$$\underset{\text{(solid)}}{Ag} \mid \underset{\text{(solid)}}{AgI} \mid \underset{\text{(solid)}}{I_2}$$

this represents a condensed system, each phase being a single substance (*no* solution or vapour being present), and we can apply Nernst's heat theorem directly in the form given in equations (1) and (2) above.

[It should be noted that the A or E of this cell is not quite the same as the E or A′ of the cell in which KI solution is present. The heat effect in both cases is, however, the same, for, as we have seen, the heat effect as calculated (say by the first method) is independent of the KI concentration, being simply the heat effect of the reaction Ag + I = AgI.]

The values of $\beta_0\nu$ and of a are known in the case of the three substances Ag, I, and AgI from the atomic and molecular heat measurements of Nernst.

By making use of the values of $\beta_0\nu$ and a obtained in this manner, Fischer calculated U for a temperature T = 288, finding the value 15,079 calories, a quantity which agrees extremely well with the former values which were obtained for U quite independently of the Nernst heat theorem, or the Nernst-Lindemann atomic heat expression. It is to be remembered that the U and A terms here refer to the reaction between pure solid Ag and solid I_2, giving solid AgI. A is therefore the affinity which we set out to calculate. The following table contains the values of A and U thus obtained:—

AFFINITY OF SILVER FOR IODINE AT VARIOUS TEMPERATURES.

Temperature, Degrees Absolute.	U in Calories per Gram-Atom of Silver.	A in Calories per Gram-Atom of Silver.
0	15,166	15,166
20	15,153	15,173
40	15,136	15,201
60	15,124	15,235
80	15,119	15,274
100	15,114	15,314
140	15,108	15,394
180	15,101	15,477
220	15,093	15,560
260	15,085	15,650
300	15,074	15,733

The accompanying figure (Fig. 12) shows diagrammatically the relative variation of U and A. It will be observed that, in this reaction, the affinity *increases* with increase in temperature, whilst the heat effect or total energy change *decreases*.

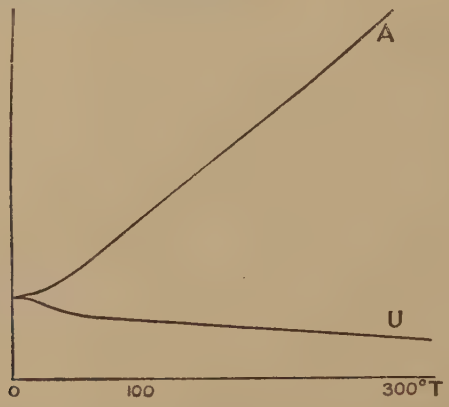

Fig. 12.

A. Magnus (*Zeitsch. Elektrochem.*, **16**, 273, 1910) has carried out a similar investigation of the reaction—

$$Pb + 2AgCl \rightarrow PbCl_2 + 2Ag$$

in which the affinity was found to *decrease* as the temperature was raised.

Mass Action Equilibrium in Solutions from the Standpoint of Infra-red Radiation.

(*Cf.* F. Krüger, *Zeitsch. Elektrochem.*, **17**, 453, 1911.)

The problem to be considered is the relation of the ionisation constant of the solute to the dielectric constant of the solvent.

The radiation density in a medium depends upon the cube of the refractive index n as well as upon other factors. Further, on the basis of the classical electro-magnetic theory of light, the refractive index is connected with the dielectric constant D by the relation $n^2 = D$. Hence the radiation density is proportional to the dielectric constant raised to the power 3/2. It follows that in media of high dielectric constant, such as water, the radiation density is correspondingly high. Thus, D for water is approximately 81, and $81^{1.5} = 730$. Hence for long waves, the radiation density in water at ordinary temperatures is 730 times the radiation density in a vacuum, where D = 1. Krüger considers the case of a dissolved electrolyte, and assumes that only a fraction of all the ions vibrate, but that those which do vibrate at all possess the theoretical amount of vibrational energy required by classical

statistical mechanics, *i.e.* 3RT per "active" gram-ion. The high dielectric constant, according to Krüger, also sets a number of the charged atoms in the undissociated molecules of the solute into vibration again with the amount of energy per "active" gram-atom [1] required by statistical mechanics. The higher the radiation density of a medium, that is, the higher its dielectric constant, the greater will be the number of molecules of solute activated in this sense, and hence the greater the degree of ionisation of the solute. This is suggested as the basis, in terms of radiation, of the relation known as the Nernst-Thomson rule.

We now pass to the consideration of the mass action equilibrium resulting from such ionisation. Krüger carries out a thermodynamic work process in which allowance is made for the difference in radiation density arising from the fact that two *different* solvents or media are employed.

Let us consider two media, dielectric constants D_1 and D_2, the media being capable of mixing in all proportions. We might imagine a cylinder containing one solvent placed above the other with a mixture layer between the two. In each solvent let us suppose that there is one gram-molecule of a binary electrolyte dissolved, the ionisation constant of the electrolyte being K_1 in solvent I. and K_2 in solvent II. ; $K_1 > K_2$. The following cyclic process is then carried out. In medium I. one mole of the undissociated electrolyte ionises. The ions are brought by the aid of semi-permeable membranes into solvent II. where they unite, the undissociated molecule being returned to solvent I. The osmotic work of transferring the *material* is as follows : let C_0, C_1, C_2 be the equilibrium concentrations of the undissociated molecules and the ions respectively of the solute in solvent I. ; C'_0, C'_1, C'_2 are the corresponding quantities in solvent II. The osmotic work of the cycle is then given by—

$$A = RT\left(\log \frac{C_1}{C'_1} + \log \frac{C_2}{C'_2} - \log \frac{C_0}{C'_0} \right) = RT \log \frac{K_1}{K_2}.$$

In this process a certain amount of radiation is absorbed when ionisation occurs in solvent I., and the same amount is given out when the ions unite in solvent II.[2] We have to deal therefore with a transport of *radiation* at the same time as we deal with a transport of material. The radiation is transported from a region of higher radiation density (solvent I.) to a region of smaller radiation density (solvent II.). The work of transporting the radiation may be calculated in the following manner :—

Let us consider a certain amount of radiation, *i.e.* the amount required to "activate" one gram-molecule of the electrolyte, and let us suppose that this radiation is enclosed in a membrane impermeable to radiation. The radiation exerts a pressure—"the pressure of light"—

[1] In the present case the "critical increment" of the undissociates molecule is very small (*cf.* Chap. VI., section dealing with Thermal Reactions).

[2] Krüger assumes here that the heat of the reaction is the same in both solvents. This, in general, will not be the case.

upon the membrane tending to expand it. This pressure is proportional to the density of the radiation. It is known that the pressure π of the radiation is related to the volume ϕ by an expression which is quite analogous to Boyle's law for gases, *viz.* $\pi\phi = k$.

[NOTE.—There is a serious difficulty here, as the expression assumes the temperature of the radiation is constant. If it is isolated its temperature cannot remain constant on expansion or compression.]

If we accept this expression it follows that the maximum work gained in expanding the radiation from π_1 to π_2, corresponding to the radiation densities u_1 and u_2, is $k \log \pi_1/\pi_2$. Further, on the electro-magnetic theory of light, $\pi = u/3$, so that the radiation work is $k \log u_1/u_2$. The density terms are proportional to the cube of the refractive indices or to the 1·5 power of the respective dielectric constants D_1 and D_2. Hence the radiation work can be written as—

$$k \log (D_1^{3/2}/D_2^{3/2}).$$

We have now to determine the constant k. "Let us assume that each vibrating ion [charged atom] in the undissociated molecule possesses three degrees of freedom, that is, each ion possesses $3/2$RT of kinetic energy and a like amount of potential energy, making in all 3RT per ion, or 6RT for the two ions in the molecule reckoned per gram-molecule—each gram-molecule when it dissociates requires on the average an amount of energy 6RT which is drawn from the radiation." Hence—

$$u\phi = 6RT,$$

and since $\pi = u/3$, it follows that—

$$\pi\phi = 2RT.$$

Substituting this in the expression for the work done in expanding the radiation, we obtain—

$$A = 2RT \log (D_1^{3/2}/D_2^{3/2}) = RT \log D_1^3/D_2^3.$$

The ionisation equilibrium is defined by the equality of the osmotic and radiation work terms.[1]

We obtain therefore—

$$RT \log \frac{K_1}{K_2} = RT \log \frac{D_1^3}{D_2^3},$$

or

$$K_1/K_2 = D_1^3/D_2^3.$$

That is, on the basis of the assumptions made by Krüger, we would expect the ionisation constant to vary as the cube of the dielectric constant of the system. In order to test this conclusion it is convenient to put it into another form. If γ_1 and γ_2 are the degrees of ionisation at the dilutions V_1 and V_2 respectively in the two solvents, then—

$$\frac{K_1}{K_2} = \frac{\gamma_1^2}{(1-\gamma_1)V_1} \cdot \frac{(1-\gamma_2)V_2}{\gamma_2^2} = \frac{D_1^3}{D_2^3}.$$

[1] Naturally if the solvent had been the *same* in both cases, and if the solutions are dilute, the radiation work term would be zero, and we are left with the osmotic work terms. The cycle would then reduce to the familiar one employed to deduce the law of mass action, *i.e.* K_1 would be identical with K_2.

If we choose the concentrations, *i.e.* the dilutions, of the solute in the two solvents in such a manner that the degrees of dissociation are the same, the above relation becomes—

$$V_2/V_1 = D_1^3/D_2^3$$

or $$D\sqrt[3]{V} = \text{constant for a given value of } \gamma.$$

This relation had already been discovered as a purely empirical one by Walden (*Zeitsch. phys. Chem.*, **54**, 129 (1906)) as a result of measurements carried out with tetra-ethylammonium iodide in a number of solvents. The following are a few of Walden's results. In each case the dilution term V denotes the dilution at which the degree of ionisation has the value assigned to it at the head of the table:—

Solvent.	Dielectric Constant.	Dilution V in Litres.	$D\sqrt[3]{V}$.
$\gamma = 0{\cdot}83$			
Water	80	32	254
Nitromethane	40	200	234
Furfurol	39	200	230
Acetonitrile	36	320	245
Methyl sulfocyanide	36	270	233
„ alcohol	32·5	400	240
Proprionitrile	27·2	800	253
Acetyl acetone	26	1000	260
Acetic anhydride	17·9	2000	226
Benzyl cyanide	16·7	3200	246
Anisaldehyde	15·5	3100	226
Benzaldehyde	14·5	4100	232
$\gamma = 0{\cdot}91$.			
Water	80	110	383
Furfurol	39	800	365
Nitromethane	40	800	371
Acetonitrile	36	1000	358
Methyl alcohol	32·5	2000	365

As will be seen, the relation is borne out approximately. Krüger deals with the possible causes of the deviations. Of these the most important is connected with the relation $n^2 = D$, which is known to hold only for very long waves. It is possible that the wave-lengths chiefly concerned in ionisation, although belonging to the infra-red region, do not conform to this relation. It is known that n varies with the wave-length when the latter is short, *i.e.* the ultra-violet, visible, and the short infra-red regions. Hence the values of D are to a considerable extent arbitrary, the values not being strictly comparable. Thus the value obtained for the dielectric constant will depend very largely on whether there exists an absorption band at the wave-length employed

in the dielectric constant apparatus. In the case of water it is considered that the high value obtained is partly due to the fact that water possesses a band for the electro-magnetic waves usually employed. Further, Krüger's assumptions are possibly not correct in all cases. Thus, it is very surprising that the results quoted should be as satisfactory as they are, for the electrolyte is *strong*. Nevertheless the deduction, so far as it goes, indicates that radiation plays a rôle in ordinary chemical processes. Krüger shows further how an empirical relationship of Walden, according to which "saturated solutions of one and the same electrolyte in various solvents possess the same degree of ionisation," can be deduced on the radiation basis. For details regarding this and other matters the original paper of Krüger must be consulted.

The Heat of Reaction. Haber's Relation.

In Chap. VI. we have dealt briefly with the rate of reaction and the velocity constant from the point of view of the quantum theory. In the case of a monomolecular reaction in a dilute gaseous system the variation of the velocity constant with the temperature is given by the expression—

$$d \log k/dT = N\hbar\nu/RT^2$$

where ν is the characteristic vibration frequency, or head of the absorption band, of the decomposing substance. If the reaction be a reversible one, the resultant being characterised by the frequency ν', the corresponding velocity constant being k', we have—

$$d \log k'/dT = N\hbar\nu'/RT^2.$$

Hence

$$\frac{d \log k/k'}{dT} = \frac{N\hbar(\nu - \nu')}{RT^2}.$$

But $k/k' = K$, the equilibrium constant. Hence we obtain the relation—

$$d \log K/dT = N\hbar(\nu - \nu')/RT^2.$$

At the same time the statistical mechanical expression of Marcelin and Rice gives the relation—

$$d \log K/dT = (E - E')/RT^2$$

where E is the critical increment of the reactant, E' that of the resultant. On comparing these expressions with the van 't Hoff isochore, *viz.*—

$$d \log K/dT = -Q_v/RT^2$$

where $-Q_v$ is the heat absorbed per stoicheiometric quantity of the reactant transformed or decomposed, we obtain the relation—

$$-Q_v \text{ (heat absorbed)} = N\hbar(\nu - \nu') = E - E'$$

or, heat *evolved* in the reaction = critical quantum of the resultant *minus* the critical quantum of the reactant.

In the case of reactions in which catalytic effects are absent we may generalise the above expression, and write—

$$\text{Heat evolved} = \Sigma N h\nu_{\text{resultants}} - \Sigma N h\nu_{\text{reactants}}.$$

This expression, deduced however by a totally different method, was first given by Haber (*Ber. Deutsch. phys. Ges.*, **13**, 1117, 1911). It may therefore be called the Haber expression for the heat effect. The above mode of deduction is that given by the writer (*Trans. Chem. Soc.*, **111**, 457, 1917).

In the above formulation the heat of reaction at constant volume has been expressed as the difference of the critical quanta or the difference of the critical increments of the resultants and the reactants. The heat effect at constant volume is also thermodynamically defined as the difference of the mean internal energies of the reactants and resultants. To see that these two definitions are concordant we may proceed in the following manner.

Let us consider the simplest type of reaction, *viz.* $A \leftrightarrows B$. The various energy terms involved in the process are represented in the accompanying diagram (Fig. 13). The ordinates denote internal energy, the length *ab* corresponding to the mean values U_1 of the internal energy possessed by one gram-molecule of the substance A, and similarly the length *de* represents the mean energy U_2 of the substance B. Before one gram-molecule of A, possessing the average internal energy U_1, can become reactive its internal energy must rise to the point *c* by the addition of the critical increment E_1. At this stage the gram-molecule possesses the energy $(U_1 + E_1)$. It may now change into one gram-molecule of B, with an evolution of energy denoted by the dotted line *ce*. The gram-molecule now possesses the mean energy *de*, or U_2 characteristic of the substance B. In passing from *c* to *e* the energy emitted is $(U_1 + E_1) - U_2$. In passing from the mean state *b* to the mean state *e* the total energy evolved is $(U_1 + E_1 - U_2) - E_1$, or $U_1 - U_2$. The total energy evolved in passing from *e* to *b* is $(U_2 + E_2 - U_1) - E_2$, or $U_2 - U_1$. This expresses the fact that if the reaction is exothermic in one direction it necessarily endothermic in the reverse direction.[1]

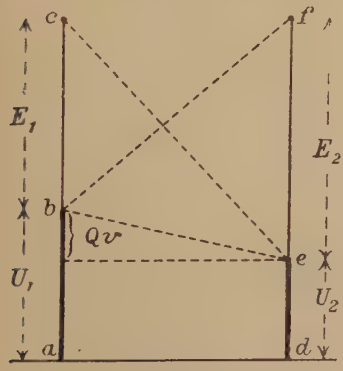

FIG. 13.

When a molecule is in the critical state it is impossible to say whether it belongs to the system A or to the system B. That is, the critical state is common to both A and B. If E_c denotes the total critical energy—not the critical increment—E_c will have the same value for the A and B molecules

[1] Note that on the above mechanism the system never passes along the line *be*.

alike. This is indicated in the diagram by the lines *ac* and *df* being of equal length. From the above considerations it follows that—

$$E_c = U_1 + E_1 = U_2 + E_2.$$

Hence $$U_1 - U_2 = E_2 - E_1 = Q_v = Nh(\nu' - \nu).$$

It will be seen that the above mechanism is somewhat more complicated than that assumed by Einstein in deducing his law of the photochemical equivalent. It agrees with Einstein's view, however, in that the energy evolutions just balance the energy absorptions when both reactions are taken into account, and therefore the radiation equilibrium is not altered when mass action equilibrium has once been attained. This assumes that the evolution from *c* to *e* is in the form of a single quantum if the absorption *ef* takes place in the form of a single quantum; and similarly for the quantities represented by *fb* and *bc* respectively.

In writing Q_v as the difference between the critical quantum of the resultant and reactant we have really assumed that Q_v is a constant independent of temperature. This, of course, cannot be exact, as it would mean that $dU/dT = o$, or that the sum of the molecular heats of reactants is equal to those of the resultants. The above radiation expression is therefore an approximation. In this connection it may be mentioned that a recent investigation of equilibria in the gaseous state has led Scheffer (*Proc. Akad. Wetenschap Amsterdam*, **19**, 636, 1917) to the conclusion that the variation in Q_v with temperature is a negligible quantity in general, *i.e.* "the experimental error in the determination of K is always such as to render meaningless any attempt to allow for the variation of Q with T". This *practical* conclusion does not affect the question, however, of the true variation of Q with T.

The integrated expression for K on the above radiation basis takes the approximate form—

$$\log_e K = -\frac{Nh(\nu - \nu')}{RT} + \text{constant}$$

or

$$\log_e K = \frac{Nh\Sigma(\nu' - \nu)}{RT} + \text{constant}$$

where ν' refers to resultants, ν to reactants, and K is so defined that the equilibrium concentration terms of the resultants appear in the numerator.

An interesting application of the above considerations suggests itself in connection with the phenomenon of fluorescence or phosphorescence. In this phenomenon we are dealing with the absorption of one type of radiation and the emission of another. The effect is regarded as due to an emission of energy which accompanies the return of an electron to its original position in the atom, the initial disturbance from this position having been brought about by absorption of radiation. According to Stokes' law the frequency of the emitted radiation is always *less* than that of the radiation absorbed. The process is therefore analogous to an endothermic change, represented in Fig. 13 by the absorption *ef* and the evolution *fb*. Stoke's law means that the process is irreversible. On the other hand, Baly (*loc. cit.*) has

made the very important discovery that the fluorescence (emission) wave-length exhibited by a substance in one solvent is identical with the absorption band exhibited by the same substance in a second solvent. That is, under one set of conditions the substance is capable of absorbing the wave-length which it emits as fluorescence under other conditions.

In the "second" solvent it is conceivable that the conditions exist for a reversal of the process (*i.e.* possibly Stokes' law is not necessarily true in general). No information is available on this point at the present time.

APPENDIX I.

Maxwell's Distribution Law and the Principle of Equipartition of Energy.

By James Rice, M.A.

The aim of mechanics is the description of motion. We seek to specify the position of every part of a system of bodies at every instant. The most direct way of doing this would be to express all the necessary geometrical co-ordinates of the system as known functions of the time. To this end the laws of motion are applied to the special features and environment of each system, and a series of differential equations are obtained which, among other quantities, involve the first and second differential coefficients of each co-ordinate with respect to the time, *i.e.* the velocities and accelerations. If the mathematician can solve for us the particular differential equations arrived at, we have attained our object for that system. Many special cases of considerable interest have proved amenable to mathematical treatment, but, at present, no solution for the general case exists.

In the phrase, "system of bodies," we must be definite as to the meaning to be attached to the word "body". In physics and chemistry, a single body is a system, *i.e.* a collection of molecules, which are in themselves discrete, if minute bodies. Indeed the molecule itself is a system of atoms, and, on present views, the atom is a system of nuclei and electrons. Even if we regard a body of fluid or solid material as a system of molecules alone, without concerning ourselves about its internal structure, the complexity of description involved in a complete account of molecular motion is so great that it becomes necessary to introduce the mathematical theory of probability. We are no longer concerned with an *exact* solution of the dynamical problem, by which one could predict with certainty the position and motion of each molecule at a given instant; instead we endeavour to find the law of distribution of the co-ordinates and velocities of the molecules, so as to be able to state, with but small possibility of error, that at a given instant such and such a fraction of the molecules will occupy such and such a portion of the space filled by the body, and have velocities lying between such and such limits. It is this feature which characterises a problem as one of statistical mechanics.

In dealing with a system of molecules, the co-ordinates referred to above are naturally the Cartesian co-ordinates of the centres of each

molecule referred to a definite set of axes; but it should be borne in mind that in general dynamics the word "co-ordinate" is used to indicate any geometrical quantity which serves to specify the position and configuration of the parts of a system, the least number of such co-ordinates which is necessary to specify the system completely being in fact its number of "degrees of freedom". Thus, if we attempt to treat the problem of a system of molecules which are themselves systems of atoms, we should have to introduce further geometrical magnitudes to those mentioned above, which would define the position of each atom relative to the centre of its corresponding molecule.

As regards the velocities of the individual molecules, there are two ways open to us to specify such a velocity, both as regards its magnitude and its direction. We may give the three components of the velocity parallel to the three axes of co-ordinates, or we may give the actual speed combined with some convenient way of indicating its direction. The following is a simple method of defining direction:—

Conceive of a sphere of unit radius. Every direction in space is parallel to some radius of the sphere. Consequently a point P on the surface of the sphere can be said to represent a direction in space, *viz.* the direction parallel to OP where O is the centre of the sphere. Any direction and its opposite are of course represented by diametrically opposite points on the sphere. In statistical work we have to classify directions into groups, and one convenient way of doing this is as follows: Draw a series of planes perpendicular to a given diameter of the unit sphere, and meeting the diameter in points which divide the diameter into an exact number, say m, of equal parts. These planes divide the surface into a series of zones, and it is well known that these zones have equal areas, *viz.* $4\pi/m$, 4π being in fact the entire area of the sphere whose radius is unity. Still further subdivide the surface by a number of planes, say n, each containing the diameter and each one making, with its neighbouring planes, angles which are all equal to an aliquot part of 2π radians, *viz.* $2\pi/n$ radian. This new family of planes cuts the surface of the sphere in great circles which subdivide each zone in equal parts, each part being four-sided and equal in area to $4\pi/mn$. (The parts round the ends of the diameter are three sided but have the same area.) If we call this area ω, then the number of such elements of area is mn or $4\pi/\omega$. It will prove convenient presently to classify directions into groups such that all the directions in one group correspond to points in one superficial element of the representative sphere. In the nature of things no finite limit can be assigned to the *number* of directions in one group, no matter how small the elements of area are made by closer and closer subdivision by the planes of "latitude and longitude," but of course closer subdivision and an increase in the number of groups involves closer and closer limits to the angular differences between any pair of directions in one group.

The problem in statistical mechanics which has received the greatest attention concerns the statistics of a body of gas enclosed in a fixed volume and in a steady state with regard to such properties as tempera-

ture pressure and density. Here, among other things, answers have been found to such questions as refer to distribution of the positions and velocities of the molecules, the mean number of molecular collisions per second, the mean free path, the connection between these quantities and the pressure, temperature, viscosity, rate of diffusion, etc., of the gas. We proceed to quote some known results concerning the distribution of the molecules in position and in velocity.

As regards the positions of the molecules, we conceive the enclosure to be subdivided into a great number, say n, "physically small" volumes or cells. This means that each cell is supposed too small to be dealt with separately by our experimental apparatus and yet large enough to contain an enormous number of molecules. As it is known that the number of molecules in one cubic mm. of a gas at N.T.P. is about 3×10^{16}, this condition is easily complied with. Suppose we have altogether N molecules in the enclosure, then the average number of molecules per cell is N/n which is assumed to be a large number. Suppose we express the actual number of molecules in any cell as $N/n \cdot (1 + \delta)$ where δ is the fractional variation of this molecular density from the mean molecular density N/n, and may be positive or negative.

It can be proved that there is an enormous probability against the possibility of δ acquiring values of an order of magnitude greater than the order of $1/N$. As N is enormous, this practically means that there is an enormous probability in favour of *uniform* distribution of the molecules in position. It should be noted as a feature of this statistical proposition that the proof of it does not prove the *impossibility* of the number of molecules in any cell deviating seriously from the mean number; it proves that such a state is extremely improbable, and that the dynamical conditions which would produce it occur so infrequently and exist for so brief a time that actual demonstration of its existence would elude our experimental arrangements.

When we come to deal with the distribution of the molecules in terms of velocity, we do not find this uniformity of distribution. Taking the question of speed alone, apart from questions of direction, there is certainly a theoretical upper limit to the possible speed attainable by any one molecule; it is in fact the speed which that molecule would have if it possessed the entire energy of the gas, the other molecules being absolutely at rest. Such a speed is, however, far beyond any practical limit; although there is no dynamical impossibility in the state of affairs pictured, there is an enormous probability against it.

The application of statistical methods to this problem leads to the view that certain speeds are more privileged than others. Thus there is one speed such that there are at a given instant more molecules possessing velocities within, say, one foot per second of this speed. than there are molecules possessing speeds within one foot per second of any other speed; and if we choose speeds smaller and smaller or larger and larger than this "maximum probability" speed, these speeds are less and less privileged, until, when we arrive at zero speed or at speeds very great compared with the maximum probability speed, the proba-

bility of their occurrence is very small indeed. There are, however, no privileged *directions*, all directions of motion being equally likely. This rough statement will serve to introduce the mathematical law of the distribution of velocities, first formulated by Maxwell and often stated in the words: "the law of distribution of the velocities among the molecules of a gas in the steady state is the law of errors".

As a matter of fact there are two ways of stating Maxwell's Law, one of which assumes a velocity to be measured by its components parallel to the Cartesian axes, the other way assumes that a velocity is to be measured by its magnitude and direction on the plan explained above (the unit sphere device). In the former case the law of the distribution is *for each component* similar to the normal law of errors, but in the latter case the law of distribution of the *speeds* is not the normal law of errors. Let us take the first method of formulation.

Considering an enormous number of molecules, N, it can be shown that in the steady state those of them which at one instant have velocities whose X components lie between narrow limits, say u and $u + du$, are in number equal to—

$$\mathrm{N}A\, e^{-\gamma u^2} du$$

where A and γ are constants to be determined shortly. This number constitutes a fraction $Ae^{-\gamma u^2}du$ of the whole. It should be carefully observed that the group of velocities here dealt with are not necessarily close to each other in magnitude and direction: it is only their X components which are close to each other in magnitude; no restriction is so far imposed on the Y and Z components.

Of this limited number there will be at the same instant a certain fraction which have their Y components between v and $v + dv$, this fraction being in fact $Ae^{-\gamma v^2}dv$; so that the number whose X and Y components are between u and $u + du$, and v and $v + dv$ respectively, is—

$$\mathrm{N}A^2 e^{-\gamma u^2} du,\ e^{-\gamma v^2} dv$$

or

$$\mathrm{N}A^2 e^{-\gamma(u^2 + v^2)} du dv.$$

A similar step gives the number of those whose X, Y, and Z components are at one instant within the limits u to $u + du$, v to $v + dv$, and w to $w + dw$ respectively, as—

$$\mathrm{N}A^3 e^{-\gamma(u^2 + v^2 + w^2)}\, du dv dw \quad . \quad . \quad . \quad (1)$$

We can calculate the constant A in terms of γ; for if we integrate for all values of u, v, and w from $-$ infinity to $+$ infinity, we must get N.

Hence $$\mathrm{N} = \mathrm{N}A^3 \int_{-\infty}^{+\infty} e^{-\gamma u^2} du \,.\, \int_{-\infty}^{+\infty} e^{-\gamma v^2} dv \,.\, \int_{-\infty}^{+\infty} e^{-\gamma w^2} dw.$$

Now it is known that the definite integral—

$$\int_{-\infty}^{+} e^{-\gamma x^2}\, dx = \sqrt{\pi/\gamma}.$$

Hence $$N = NA^3(\sqrt{\pi/\gamma})^3.$$

Hence $$A = \sqrt{\gamma/\pi}.$$

We can also calculate γ in terms of the total kinetic energy of the molecular motion. For the fraction of the whole, *i.e.* fractional number of the whole number of molecules, which is represented by—

$$NA^3 e^{-\gamma(u^2+v^2+w^2)}\,dudvdw$$

have each kinetic energy $\frac{1}{2}m(u^2 + v^2 + w^2)$ where m is the mass of a molecule.

Hence the total kinetic energy is—

$$\tfrac{1}{2}NA^3 m \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw \,.\, (u^2+v^2+w^2) \,.\, e^{-\gamma(u^2+v^2+w^2)}\,dudvdw$$

Leaving aside the constant factor for the moment, we see that the triple integral is the sum of three triple integrals, one of which, for instance, is—

$$\int_{-\infty}^{+\infty} u^2 e^{-\gamma u^2} du \,.\, \int_{-\infty}^{+\infty} e^{-\gamma v^2} dv \,.\, \int_{-\infty}^{+\infty} e^{-\gamma w^2} dw.$$

Now it is known that—

$$\int_{-\infty}^{+} u^2 \,.\, e^{-\gamma u^2} du = \tfrac{1}{2}\sqrt{\pi/\gamma^3}$$

and the two remaining integral factors in the above chosen integral have already been evaluated. Hence the selected member of the three triple integrals has the value $\frac{1}{2}\sqrt{\pi^3/\gamma^5}$, and the other two have each the same value. Hence the total kinetic energy is—

$$\tfrac{3}{4}NA^3 m\sqrt{\pi^3/\gamma^5},\ \textit{i.e.}\ \tfrac{3}{4}Nm/\gamma;\ \text{since } A = \sqrt{\gamma/\pi}.$$

Now we could conceive the molecules all moving with one uniform velocity as a rigid body, for instance, and that velocity such as to give the same kinetic energy as that due to the gaseous motion. Denote the magnitude of this hypothetical velocity by $\bar{c}$, and we have—

$$\tfrac{1}{2}Nm\bar{c}^2 = \tfrac{3}{4}Nm/\gamma,$$

or $$\gamma = 3/2\bar{c}^2.$$

This particular speed $\bar{c}$ is not the true average speed, nor is it the maximum probability speed referred to above (its relation with these will be given presently); it is in fact a speed whose square is the average of the squares of the molecular speeds at one instant, and on that account is called the root-mean-square or r-m-s-speed. Assuming that this r-m-s-speed is known, we formulate Maxwell's Law in one way thus :—

Of a great number N of gaseous molecules in a steady state with an r-m-s-speed $\bar{c}$, the number whose velocity components at one instant lie between the limits u to $u + du$, v to $v + dv$, w to $w + dw$, is—

$$N \,.\, \sqrt{\frac{27}{8\pi^3\bar{c}^6}} \,.\, e^{-3(u^2+v^2+w^2)/2\bar{c}^2}\,dudvdw \quad . \quad . \quad . \quad (2)$$

and we see that any one particular component, say u, enters into this expression in a manner similar to the way the error x enters into the expression for the normal law of errors, *viz.* $\int e^{-h^2x^2}dx$.

We can employ a geometrical method of representing this law. Imagine that u, v, w, are chosen to be the Cartesian co-ordinates of a point in a three dimensional diagram, which we will refer to as the velocity diagram. The origin O of the co-ordinates in this diagram represents absolute rest, while any other point P represents a velocity whose magnitude is given by the length OP and whose direction is the direction of OP. Let us write c for the length OP, *i.e.*—

$$c(= \sqrt{u^2 + v^2 + w^2})$$

gives the actual speed corresponding to the point P. Now suppose we represent, as it were, every molecule by a point in this diagram, *i.e.* each point represents the velocity—not the position—of some molecule, so that we have therefore N points marked in the diagram; these points will, of course, move about with lapse of time, because of the changing velocity of the corresponding molecule. The expression (2) states the volume distribution of these points at a given instant. Thus, taking $dudvdw$ to be an element of volume of the velocity diagram the "density" of the points around the point representing zero speed, *i.e.* representing the condition of rest, is—

$$N\sqrt{27/8\pi^3\bar{c}^6}.$$

Around any point representing a speed c (with no restriction as to direction), *i.e.* around a point lying anywhere on a sphere of radius c with its centre representing rest, the density of the points is—

$$N\sqrt{27/8\pi^3\bar{c}^6}\,.\,e^{-3c^2/2\bar{c}^2} \quad . \quad . \quad . \quad . \quad (3)$$

So the density of the swarm of points diminishes in this exponential manner as we recede from the point representing rest. The reader is warned against drawing the erroneous conclusion that there are at any moment more molecules in the gas at rest, or very nearly so, than there are those possessing any other assigned speed or near to it. The fallacy involved in such an inference will be pointed out presently.

An element of volume in the velocity diagram represents what is called an "extension-in-velocity," just as an element of volume in actual space occupied by a gas is an "extension-in-position". Thus we may refer to expression (3) as the "density-in-velocity" of the molecules about any velocity of the magnitude c.

We can readily pass to the second manner of formulating Maxwell's Law, and in so doing clear away the possibility of misconception referred to a few lines back. Suppose we wish to find the number of molecules whose *speeds* (*i.e.* merely velocity magnitudes) are at any moment between the limits c and $c + dc$, but with no limits placed on their directions of motion. We must obviously find the number of points in our velocity diagram which lie between spherical surfaces of radii c and $c + dc$. The volume of the elementary region of this diagram is $4\pi c^2 dc$,

and the point density in the region is given by (3). Hence the number sought is—

$$4\pi N \sqrt{27/8\pi^3\bar{c}^6} \cdot c^2 e^{-3c^2/2\bar{c}^2} \cdot dc \quad . \quad . \quad . \quad (4)$$

The expression (4) has, for a given value of the differential element of speed, dc, its maximum value for a value of c which makes—

$$c^2 e^{-3c^2/2\bar{c}^2}$$

a maximum. By the usual methods of the calculus it appears that this value of c is: $\sqrt{\frac{2}{3}}\bar{c}$ or $0{\cdot}816\bar{c}$; so that there are more molecules at an instant possessing speeds within, say, one foot per second of this speed than of any other assigned speed. That is, $0{\cdot}816\bar{c}$ is the speed with "maximum probability".

We can now deal with the fallacious inference mentioned above. Let us consider a velocity with speed c and a *definite* direction whose direction angles are α, β, and γ. The velocity has then the components—

$$c \cos \alpha,\ c \cos \beta,\ c \cos \gamma.$$

Now, undoubtedly, there are more molecules whose velocities have components between o, o, o and du, dv, dw than there are molecules with velocity components between $c \cos \alpha$, $c \cos \beta$, $c \cos \gamma$ and $c \cos \alpha + du$, $c \cos \beta + dv$, $c \cos \gamma + dw$. This is a just inference from equation (3); but this statement is not true if we remove the condition of *definiteness* from the angles α, β, and γ and allow them to take any possible values. The removal of this restriction does not alter the *speed* limits, but it multiplies the number in the second group enormously. From the point of view of the velocity diagram, the representative points do undoubtedly cluster more densely around the origin of the diagram, and less and less densely around a point gradually receding from the origin, but the actual law of distribution provides for the number of points which lie in a thin spherical shell of definite thickness, increasing as we go out to a shell of average radius $0{\cdot}816\bar{c}$ and then decreasing as we go still further. From the origin to $0{\cdot}816\bar{c}$, the increasing volume of the shell more than compensates the decreasing density of the points; further on it fails to do so.

We can modify expression (4) so as to deal with velocities having defined limits of direction. Expression (3) shows us that the density-in-velocity is a function of speed only; hence there are no privileged directions. So of those molecules which at an instant have speeds between c and $c + dc$, the number whose directions of motion are restricted to the directions represented by points on a superficial element ω of the unit sphere constitute a fraction $\omega/4\pi$. Multiplying expression (4) by this fraction, we find that the number of molecules so restricted as to speed and direction is—

$$\omega N \sqrt{27/8\pi^3\bar{c}^6} \cdot c^2 \cdot e^{-3c^2/2\bar{c}^2} \cdot dc \quad . \quad . \quad . \quad (5)$$

If we wish to find the number of molecules which have speeds within limits finitely separated we must integrate (4) or (5) between the limits.

Thus the number, unrestricted as to direction, with speeds between c_1 and c_2, is—

$$4\pi N \sqrt{27/8\pi^3 \bar{c}^6} \int_{c_1}^{c_2} c^2 . e^{-3c^2/2\bar{c}^2} . dc \quad . \quad . \quad . \quad (6)$$

Expression (6) can be much simplified by introducing instead of the speed c the ratio which this speed bears to the maximum probability speed $\sqrt{\frac{2}{3}} . \bar{c}$.

Call this ratio x so that—

$$c = \sqrt{\tfrac{2}{3}} . \bar{c} . x$$

and hence

$$dc = \sqrt{\tfrac{2}{3}} . \bar{c} . dx.$$

On introducing these expressions into (6) we find after a little rearrangement that the number of molecules whose speed ratios lie between x_1 and x_2 is—

$$4N/\sqrt{\pi} . \int_{x_1}^{x_2} x^2 e^{-x^2} dx \quad . \quad . \quad . \quad . \quad (7)$$

[In (7) we might refer to x as the speed, if we took the maximum probability speed as the unit of speed.]

The properties of the integral in (7) can be most readily exhibited by means of Fig. 14, which is the graph of the curve—

$$y = x^2 e^{-x^2}$$

The graph begins at the origin O; y rises to a maximum value $1/e$ (or

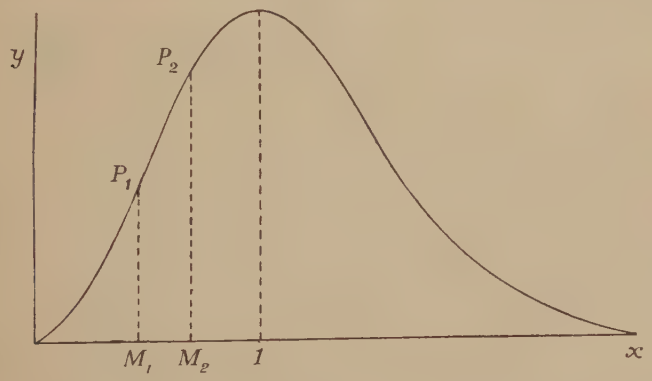

FIG. 14.

0·37 approximately) when $x = 1$; the curve then descends asymptotically to the axis of x, y reaching as low a value as 0·02 when $x = 2·5$, showing that all but a very small fraction of the molecules have speeds at any moment less than two and a half times the maximum probability speed (which corresponds to x equal to unity) or practically twice the r-m-s-speed. In fact, the fraction of the molecules whose speed ratios

lie between x_1 and x_2 is given by: $4/\sqrt{\pi}$ area of $P_1M_1M_2P_2$, where $OM_1 = x_1$ and $OM_2 = x_2$. By methods of analysis or quadrature of a carefully drawn graph numerical values can be obtained. The following table from Meyer's *Kinetic Theory of Gases* (translated by Baynes) illustrates the point:—

Of 1000 molecules of oxygen at 0° C., whose r-m-s-speed is known (by methods to be explained presently) to be 461·2 metres per second—

13 to 14	molecules	have	speeds	below	100 to 200	metres	per	second.
81 ,, 82	,,	,,	,,	from	200 ,, 300	,,	,,	,,
166 ,, 167	,,	,,	,,	,,	300 ,, 400	,,	,,	,,
214 ,, 215	,,	,,	,,	,,	400 ,, 500	,,	,,	,,
202 ,, 203	,,	,,	,,	,,	500 ,, 600	,,	,,	,,
151 ,, 152	,,	,,	,,	,,	600 ,, 700	,,	,,	,,
91 ,, 92	,,	,,	,,	,,	above 700	,,	,,	,,
76 ,, 77	,,	,,	,,					

The table shows that all but about 10 per cent. of the molecules have speeds between one-half and double the r-m-s-speed. It thus appears that despite the possibility of any definite molecule acquiring a speed enormous in comparison with the average, the probability of it doing so is exceedingly remote. It should also be observed in illustration of the point dealt with earlier, that the number possessing quite low speeds is also very small.

The kinetic theory of gases explains the pressure of a gas as the result of molecular bombardment, and connects the pressure and temperature of the gas with its mean molecular kinetic energy. The actual relations are as follows:—

If ρ grams per c.c. is the density of the gas, and p dynes per square cm. its pressure, it can be shown that—

$$p = \frac{1}{3}\rho\bar{c}^2$$

where $\bar{c}$, the r-m-s-speed, is measured in cms. per second. If p and ρ are known, this enables us to calculate $\bar{c}$, as, for example, in the table just given. If E is the energy of motion of a molecule—

$$E = \tfrac{1}{2}mc^2$$

where m is the mass of a molecule; and if $\overline{E}$ is the mean molecular kinetic energy, then—

$$\overline{E} = \tfrac{1}{2}m\bar{c}^2.$$

Hence

$$p = \tfrac{1}{3}nm\bar{c}^2 = \tfrac{2}{3}n\overline{E}$$

where n is the number of molecules per c.c.

The experimental gas laws are summarised in the statement that—

$$pv = RT$$

where v c.c. is the volume of one gram-molecule of the gas under the pressure p at the temperature T and R is the gram-molecular gas constant.

Hence we derive—

$$\frac{2}{3}nv\bar{E} = RT, \text{ or } \bar{E} = \frac{3}{2} \cdot \frac{R}{nv} \cdot T.$$

But nv is the number of molecules in the gram-molecule; so R/nv is the gas constant per molecule, usually denoted by k. Thus we obtain, as the connection between the temperature of the gas and its mean molecular motion—

$$\bar{E} = \tfrac{3}{2}kT \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We have so far dealt with a gas composed of similar molecules, but if we consider a gas mixture containing molecules of different masses, little alteration is required in the formulæ. It can be shown that among each group of molecules of one type, the relative distribution in speed and direction is similar to that already outlined for a simple gas, and is unaffected by the presence of other types of molecules. This is a statistical generalisation of the well-known law of Dalton concerning gas mixtures. Thus, each group of molecules has a certain r-m-s-speed, but the value of this varies from group to group; however, a very simple relation connects them. If we denote types of molecules by suffixes, 1, 2, 3, etc., then—

$$m_1\bar{c}_1^2 = m_2\bar{c}_2^2 = m_3\bar{c}_3^2 = \text{etc.}$$

where m_1, m_2, m_3, etc., are the masses of each type of molecule. In terms of average kinetic energies per group of molecules this is—

$$\bar{E}_1 = \bar{E}_2 = \bar{E}_3 = \text{etc.}$$

Referring to (8) we see that this dynamical conclusion is the statistical statement of the equality of temperature which obtains throughout the gas mixture when a steady state has been attained. On account of this relation it becomes more convenient to state the distribution law in terms of limits of kinetic energy. This is easily done. Thus, reverting to the case of a simple gas for a moment, we introduce the following changes into (4):—

Write

$$E = \tfrac{1}{2}mc^2$$
$$\bar{E} = \tfrac{1}{2}m\bar{c}^2$$
$$dE = mc \, . \, dc$$

and we obtain after a few steps—

$$4\pi N\sqrt{\frac{27}{3^2\pi^3\bar{E}^3}} \, . \, E^{\frac{1}{2}} \, . \, e^{-3E/2\bar{E}}dE$$

as the number of molecules with kinetic energies between E and E + dE at an instant.

We may avail ourselves of (8) and obtain instead of this expression the following one:—

$$\frac{2N}{\sqrt{\pi k^3T^3}} \, . \, E^{\frac{1}{2}} \, . \, e^{-E/kT} \, . \, dE \quad . \quad . \quad . \quad (9)$$

as the number of molecules limited in the manner mentioned.

Now it can be shown that for a gas mixture consisting of N_1 molecules of type 1, N_2 molecules of type 2, etc., in a steady state, and therefore with the same mean energy of motion (*i.e.* the same temperature) throughout, the number of molecules of type 1, of type 2, etc., within the defined limits of kinetic energy are given by expression (9), with N replaced by N_1, N_2, etc., in succession. Briefly, the distribution of kinetic energy ignores differences in molecular mass.

Hitherto we have considered the gas to be free from all external forces such as gravity, and subject only to the forces arising from collision with each other or with the comparatively fixed molecules in the solid walls of the containing vessel. If we introduce external forces of a conservative type the previous formulæ must be modified as follows :—

Denote the co-ordinates of a point in the gas as X, Y, Z; the potential energy of a molecule *m* of the gas at this point is a function of X, Y, Z; call it χXYZ or simply χ.

We no longer have a uniform density of distribution in *position* for the molecules. The density, in fact, diminishes as we move to places of greater potential energy. A good illustration of this is the progressive decrease in the density of the atmosphere as the altitude increases. It can be shown that the molecular density is proportional to—

$$e^{-\chi/kT}.$$

Hence, the number of molecules in an element of volume *dx*, *dy*, *dz* at the point XYZ is—

$$ne^{-\chi/kT}dxdydz$$

where *n* is a constant. As a matter of fact *n* is the molecular density in a small volume surrounding a point where the potential energy, χ, is zero.

The distribution in kinetic energy of the molecules in this element of volume is just as before. Hence we can write in full—

$$\frac{2n}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} e^{-(E+\chi)/kT} dE \cdot dxdydz \qquad . \quad . \quad (10)$$

as the number of molecules in an element of volume *dxdydz*, where the potential energy of a molecule is χ, and whose kinetic energies lie between E and E + *d*E.

The extension of this result to the case of a gaseous mixture is easily given. Let the potential energies of each type of molecule in the external field of force at the point XYZ be χ_1, χ_2, χ_3, etc.; then the numbers of each type of molecule in the volume element *dxdydz*, at this point limited as in (10), are—

$$\left.\begin{aligned} &\frac{2n_1}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} \cdot e^{-(E+\chi_1)/kT} dE dxdydz \\ &\frac{2n_2}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} \cdot e^{-(E+\chi_2)/kT} dE dxdydz \end{aligned}\right\} \qquad . \quad . \quad (11)$$

and so on.

Here n_1, n_2 are the molecular densities of each type of molecule around a point where the potential energy is zero.

The formulæ developed hitherto have postulated implicitly an *absence* of intermolecular forces, except such as arise in a collision between molecules, an event which, though *absolutely* very frequent for a molecule, is *relatively* rare, since the time which a molecule spends in its free paths is very much larger than the time spent in collisions. When we introduce intermolecular forces, *i.e.* when we approach the liquid or solid state, the formulæ become more complex, and as they are not required in the text of the chapter to which this appendix refers, may be laid aside.

A more important case for our purpose is the case of a gas whose molecules can no longer be considered as simple rigid bodies, but for which an atomic and even a sub-atomic structure must be postulated. It would take us too far afield to treat the formulæ for this case in all their generality, but we can deal with a few statements of service later.

As before, we take the number of molecules as N, and consider that the general position of each molecule is given by the three Cartesian co-ordinates of its centre of mass. Besides these three co-ordinates there are other geometrical quantities (or co-ordinates in a more general sense) necessary to define the structure of a molecule. These *internal* co-ordinates can be most readily thought of as the *least* number of lengths and angles necessary to specify the position of every distinct and conceivably separate part of the molecule with regard to its centre of mass. The number of these co-ordinates constitute the internal "degrees of freedom" of the molecule. Suppose there are n of them, the necessary n co-ordinates being denoted by the letters—

$$q_1\ q_2\ \ldots\ q_n.$$

The rates of change of these co-ordinates as the molecular parts move relatively to one another are referred to as "components of velocity" or simply "velocities," each corresponding to a definite degree of freedom. Writing $\dot{q}$ for dq/dt, these velocities are—

$$\dot{q}_1\ \dot{q}_2\ \ldots\ \dot{q}_n.$$

As the parts of the molecule act on each other by means of interatomic and intra-atomic forces (of electric origin), the molecule possesses a certain amount of internal potential energy, as well as a certain amount of internal kinetic energy due to the motions of the parts relative to the centre of the mass. This kinetic energy can be expressed as a quadratic function of the velocities $\dot{q}_1\ \ldots\ \dot{q}_n$. The case which has been most extensively treated, and which is very amenable to mathematical analysis, permits of the potential energy also being expressed as a quadratic function of the co-ordinates $q_1\ \ldots\ q_n$. This assumption is possible when we have to deal with the *small* oscillations of the various parts about positions of relative equilibrium, or about states of steady relative motion, and these conditions have thrown a great deal of light, *e.g.* on the radiating mechanisms of molecules. It

is possible with this assumption so to chose the co-ordinates that the total internal energy, kinetic *and* potential, involves only squares of the co-ordinates and velocities, so that we can write the *total* internal energy ϵ as—

$$\epsilon = a_1\dot{q}_1^2 + \ . \ . \ . \ + a_n\dot{q}_n^2 + b_1q_1^2 + \ . \ . \ . \ b_nq_n^2$$

where $a_1 \ . \ . \ . \ a_n$, $b_1 \ . \ . \ . \ b_n$ are constants.

In this manner and under the conditions laid down we can, as it were, partition the energy among the various degrees of freedom, $a_1\dot{q}_1^2$ being, for example, the kinetic energy "belonging to" the first degree of freedom, and $b_1q_1^2$ the potential energy belonging to the same degree of freedom, and so on. There is in addition, of course, the kinetic energy of translation of the molecule as a whole, *viz.* $\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2$, which we will write as K (kappa) involving three more degrees of freedom, with the energy as before partitioned between the three degrees.

We can now state some results of the application of statistical mechanics to a system of such molecules. It must be understood, however, that these results rest on the validity of the classical dynamics. Of late these results have been impugned by Planck and others, and the foundations of dynamics are undergoing a revision. It will, however, enable the reader to grasp the modifications proposed if he masters the following few statements and accepts their truth at all events provisionally.

As the molecule moves about and its parts oscillate with regard to each other, its energy changes, not only *in toto* but also in its several terms. It can be shown, however, that the mean energy, kinetic *or* potential, belonging to any co-ordinate, averaged over a considerable period of the molecule's history, is the same for all the degrees of freedom and is equal to $\frac{1}{2}k\mathrm{T}$. That is—

$$\overline{\tfrac{1}{2}m\dot{x}^2} = \overline{\tfrac{1}{2}m\dot{y}^2} = \overline{\tfrac{1}{2}m\dot{z}^2} = \overline{a_1\dot{q}_1^2} = \overline{a_2\dot{q}_2^2} = \ . \ . \ . \ = \overline{b_1q_1^2} = \overline{b_2q_2^2} = \ . \ . \ . \ = \tfrac{1}{2}k\mathrm{T}.$$

This is a statement of the famous theorem due to Maxwell and usually referred to as the "equipartition of the energy among the various degrees of freedom".

Further, it can be shown, as before, that the number of molecules which have velocities between *uvw* (*i.e.* $\dot{x}\dot{y}\dot{z}$) and $u + du$, $v + dv$, $w + dw$ is—

$$\mathrm{A} \ . \ \mathrm{N} \ . \ e^{-\kappa/k\mathrm{T}} \ . \ dudvdw \qquad . \quad . \quad . \quad (12)$$

where A is a constant.

Of this limited number a still more limited number exists at one instant whose several total internal energies, kinetic *and* potential, lie between ϵ and $\epsilon + d\epsilon$.

This latter number forms a fraction of the former whose value is—

$$\mathrm{B}\epsilon^{n-1}e^{-\epsilon/k\mathrm{T}}d\epsilon \ . \qquad . \quad . \quad . \quad . \quad (13)$$

where B is a constant.

Combining the two expressions, we have the number whose internal

energies lie between ϵ and $\epsilon + d\epsilon$, and whose general velocities of translation lie between uvw and $u + du$, $v + dv$, $w + dw$, as—

$$C \cdot N \cdot \epsilon^{n-1} \cdot e^{-(\epsilon+\kappa)/kT} d\epsilon du dv dw \quad . \quad . \quad . \quad (14)$$

where C is a constant.

As an important particular case, expression (13) reduces for one *internal* degree of freedom to—

$$Be^{-\epsilon/kT} d\epsilon \quad . \quad . \quad . \quad . \quad (15)$$

Equation (15) forms the basis of the expression of Marcelin and Rice for the rate of decomposition of a molecule referred to in Chapter VI. under the heading "Reaction velocity from the standpoint of the quantum theory". The expression for the velocity constant on the basis of statistical mechanics is given by Rice (*Brit. Ass. Report*, 1915, p. 397).

APPENDIX II.

Foundations of the Quantum Theory.

By J. Rice, M.A.

(From the *Transactions of the Faraday Society*, xi., p. 1, 1915.)

During the nineteenth century certain facts had been well established concerning the radiation contained in an enclosure maintained at constant temperature. Balfour Stewart and Kirchhoff had shown that if the material of the walls was not perfectly reflecting for any quality of radiation, any constituent of the radiation having a definite frequency was present in an amount depending on that frequency, the temperature and size of the enclosure, but independent of the nature of the wall-material. Stefan and Boltzmann had proved that the energy of the total radiation in one c.c. was proportional to the fourth power of the absolute temperature. Wien had reached the conclusion that the energy-density of those constituents of the radiation, whose wave-lengths lay between narrow limits λ and $\lambda + \delta\lambda$, was $\frac{f(\lambda T)}{\lambda^5}\delta\lambda$, where the function f in the numerator, although undetermined in form, was dependent on the single variable λT, the product of the wave-length and the absolute temperature. These statements had been arrived at by reasoning of a purely thermodynamic nature, based on the existence of a radiation pressure. It was only natural that the statistical methods, already employed as a successful weapon of attack on problems arising out of the kinetic theory of gases, should be presently pressed into service in this new line of research. There is some resemblance between a vessel containing molecules, individually uncontrollable but maintaining a certain average condition of energy by encounters, and an enclosure maintaining a statistically permanent condition of radiation by the emission and absorption of its walls, while the history of any particular wave-train of definite frequency cannot be followed in detail. There is one marked difference between the two cases: molecules can, by direct encounter with each other, as well as by collision with the walls, exchange energy; but in a temperature enclosure passage of energy from one wave-train to another must take place through the agency of the walls alone or of matter contained within them, since two such trains can pass through the same element of volume (*i.e.* cross one

another without any change in the energy or quality of the trains). For this reason, if the walls are perfectly reflecting, any arbitrary condition of radiation supposed existing at one moment would remain permanently unaffected in the energy and quality of its constituents, and only by the introduction of a piece of non-reflecting matter into the enclosure could the radiation be gradually brought to the condition of "full" or "complete" radiation for the temperature, the condition considered by Balfour Stewart and Kirchhoff.

Wien, himself, had made an attempt to determine the form of the function in the numerator of his so-called displacement formula.[1] He considered the enclosure to contain a perfectly absorbing or "black" body, which he assumed to be a gas with its molecules distributed according to the Maxwell Law, and its temperature therefore proportional to the mean-squared velocity. A further hypothesis (a very doubtful one) was the assumption that those molecules whose velocities lie within certain narrow limits at a definite instant are at that instant emitting light within narrow frequency limits, with an intensity proportional to the number of those molecules. By these means Wien arrived at the form $e^{-\frac{c}{\lambda T}}$ for his function $f(\lambda T)$, c being a constant. Measurements carried out shortly after by Lummer and Pringsheim, Beckmann, and Rubens verified the formula as a good representation of the facts for short wave-lengths, but found it completely at variance with the facts for long wave-lengths.

It was by the application of statistical principles in another direction that the next advance towards a correct radiation formula was made. Wien had considered the molecules of the black body. Lord Rayleigh, and afterwards Jeans, considered the radiation itself, assigned co-ordinates to it and "degrees of freedom," and applied the results of Maxwell's distribution law directly to these concepts. Such applications are certainly rather easier to apprehend "physically" in the case of gas molecules than in that of constituent wave-trains of radiation; there is more "substantiality" about a molecule than a wave-train. The representation of a molecule as a small, hard sphere with perfect resilience, which is quite adequate for many purposes, and analogies with billiard-balls, discs, etc., put one on fairly familiar terms with molecular motion and exchange of energy. The degrees of freedom of such simple systems are easily calculable, being in fact six for a "rigid" molecule of any shape. Even if we introduce atomic structure into the molecules, the degrees can still be computed if one knows the parts and their connections. The energy of the system at a given temperature is then obtained by the principle of equipartition, which is derived from the law of distribution, and asserts that the kinetic energy can be calculated by assigning to each degree of freedom an amount $\frac{1}{2}k\mathrm{T}$ ergs, where k is the molecular gas constant ($1{\cdot}35 \times 10^{-16}$ ergs/degrees), an equal amount of potential energy being also assigned to any degree of freedom, if there are "elastic" forces of the usual simple harmonic type.

[1] *Wied. Ann.*, 58, p. 662, 1896.

If such ideas are to be generalised and extended to the ether of an enclosure, a definite notion as to the structure of the ether is imperative before any headway can be made in calculating its degrees of freedom. At the outset it is fairly evident that the usual conception of the ether as a perfectly continuous medium indivisible into an enumerable number of discrete parts, should lead to an infinite number of degrees of freedom, with the resulting conclusion that in a state of equilibrium the ether in the enclosure should contain all the energy and the walls none. The well-known illustration of the gradual loss of vibratory energy from the particles of a sounding body to the surrounding air may serve to make this point clearer. This conclusion is in fact reached by the Rayleigh-Jeans analysis, and is very much at variance with the facts as we know them. The formula arrived at, however, is a close approximation to the truth for long wave-lengths, and the calculation of the number of degrees of freedom has proved of signal service in itself. It is impossible to reproduce the analysis here, but an analogy from sound waves may serve to show the principles on which it is based. It is well known that an organ-pipe will resound only to notes of definite frequencies, the fundamental and its overtones. This is due to the fact that any state of "stationary" wave-motion which will persist in the air of the pipe has to satisfy certain end conditions—*e.g.* at a closed end there can be no vibratory motion of the air particles, at an open end no change of pressure. Any text-book on sound shows that from these conditions there can exist in a very narrow pipe, closed at both ends or open at both ends, only waves whose wave-lengths are $2l$, $\frac{2l}{2}$, $\frac{2l}{3}$ . . . $\frac{2l}{n}$, etc., where l is the length of the pipe. The frequencies are, of course, $\frac{v}{2l}$, $2\frac{v}{2l}$, $3\frac{v}{2l}$ . . . $n\frac{v}{2l}$, etc., where v is the velocity of sound. Now if we write ν for $n\frac{v}{2l}$, we see that the number of possible modes of vibration whose frequencies are not greater than ν is $n = \frac{2l}{v} \cdot \nu$. Remembering that this is the result for a narrow pipe in which the wave-motion is parallel to one direction, let us extend the method to a flat shallow box, enclosed between two square ends so that the wave-motion takes place in any direction lying in one of the ends. The number of modes of vibration having ν as the upper limit of their frequencies would now be proportional to $\left(\frac{2l}{v} \cdot \nu\right)^2$, a result not difficult to apprehend, since we can in a rough sort of way suppose that with any one type of wave-motion parallel to one edge of the flat ends, we can compound any of the types which can exist parallel to the rectangular edges so as to obtain a possible wave-train travelling obliquely round and round the box, reflected

continuously from the narrow long faces which also bound the box. If we still further extend these considerations to a cubical box, the number of possible modes come out to be proportional to $\left(\frac{2l}{v} \cdot \nu\right)^3$, *i.e.* to $8\frac{\tau}{v^3} \cdot \nu^3$, τ is the volume of the box. A differentiation shows that the number of possible modes which lie between narrow limits of frequency ν and $\nu + \delta\nu$, is $24\frac{\tau}{v^3} \cdot \nu^2\delta\nu$. As a matter of fact a complete analysis shows that the numerical factor should be 4π and not 24. Now the point of this analogy lies in the fact that whatever be the nature of a beam of radiant energy, a certain definite condition has to be obeyed at a perfectly reflecting surface—on the electro-magnetic theory the tangential component of the electric intensity in the wave must be zero there—and this condition limits the number of types of radiation wave-trains which can persist unchanged as stationary waves in an enclosure with reflecting walls. Consequently, if we introduce a small portion of perfectly absorbing matter into a cube with perfectly reflecting walls, we can assert that, despite the fact that the matter can radiate and absorb any type of radiation, only those types will exist in the final state of equilibrium which satisfy the boundary conditions referred to above, just as our box organ-pipe would not resound to every small whistle introduced into it, but only to a whistle having one of a definite series of pitches. These types of radiation will constitute complete radiation at the temperature, since experiment has certainly justified Kirchhoff's conclusion that the frequencies and energies of the constituents of radiation in a temperature enclosure are independent of the size or nature or shape of the walls, so long as there is present a portion of non-perfectly reflecting matter. The number of types of radiation, therefore, which exist in full radiation, having frequencies between the narrow limits ν and $\nu + \delta\nu$, would appear to be $4\pi\frac{\tau}{c^3} \cdot \nu^2\delta\nu$, where c is the velocity of light; but, as a matter of fact, this number has to be doubled, since radiation waves are transverse to the direction of propagation (not longitudinal to it, as in the case of sound waves), and therefore any particular wave has to be regarded as due to the composition of two waves of the same period and phase, each polarised in one of two definite rectangular planes. So the final result for the number is $\frac{8\pi\tau}{c^3}\nu^2\delta\nu$. This means that in order to specify the electro-magnetic condition (electric and magnetic intensities) at any assigned point in the ether of the box, at any assigned instant, expressions involving a number $\frac{8\pi\tau}{c^3}\nu^2\delta\nu$ of terms each varying harmonically with the time would be required to designate that part of the effect due

to waves of frequencies in the range ν, $\nu + \delta\nu$. This number is in fact the number of independent co-ordinates or degrees of freedom for such qualities of radiation. Ascribing the usual kT units of kinetic and potential energy to each degree, we obtain for the energy of radiation in the range ν, $\nu + \delta\nu$, the amount $\frac{8\pi\tau}{c^3}kT\nu^2 . \delta\nu$ ergs, or for the energy-density, $\frac{8\pi}{c^3}kT\nu^2 . \delta\nu$ ergs per c.c. In terms of wave-lengths we obtain by putting $\nu = \frac{c}{\lambda}$ and $\delta\nu = -\frac{c}{\lambda^2}\delta\lambda$, that the energy-density of radiation whose wave-lengths lie in the range λ, $\lambda + \delta\lambda$ is $\frac{8\pi kT}{\lambda^4}\delta\lambda$ ergs per c.c.[1]

It is an obvious drawback to the Rayleigh-Jeans expression that it does not approach a finite limit, as λ decreases to zero. In fact, the ether would appear to contain an infinite amount of energy per c.c. since—

$$\int_{\infty}^{0} \frac{d\lambda}{\lambda^4}$$

is certainly infinite.

We might evade this objection by observing that exchange of energy from one type to another must be effected by the material of the enclosure (as was pointed out above), and that we might reasonably suppose the radiating mechanisms in the atoms to be of such a nature that they could not emit radiation of a quality higher than a certain limiting frequency, and so the upper limit of the integral would be a finite quantity and not zero. But this would not meet the difficulty that for the same amount of range in wave-lengths $\delta\lambda$, there is a greater contribution to the energy density from high-grade qualities than from low-grade, according to the Rayleigh-Jeans formula; whereas experiment shows that the factor of $\delta\lambda$ exhibits a maximum value for a certain wave-length λ_m (dependent on temperature), and approaches zero as a limit as λ approaches zero or infinity.

It has been suggested that the tendency, expressed in the Rayleigh-Jeans Law, of the radiation energy to pass more and more into the higher qualities, is in reality a true phenomenon of nature, and that we fail to appreciate it in our experimental tests because all temperature enclosures fail to confine the energy of the highest frequencies; such energy leaks out, as it were, through the walls and through the small opening facing the radiometer, almost as fast as it is supplied from low-frequency radiation by the agency of the walls; and so the condition we actually observe is a compromise—a stage on the way to the final consummation expressed in the ideal formula, but unattainable except after an enormous

[1] *Phil. Mag.*, **49**, 539, 1900; **10**, 91, 1905; **17**, 229, 1909. *Nature*, **72**, p. 94 and p. 243, 1905.

lapse of time. The difficulty of accepting this suggestion is the difficulty of believing that such a compromise should be found to be so completely independent of the nature of the walls as experiment demonstrates. The formula, however, does agree with fact very well for long wave-lengths, just as Wien's does for short.

Faced with this discrepancy, there are two alternatives which offer themselves as obvious methods of escape from it. We may deny the validity of the calculation of the degrees of freedom, or we may urge objections to the law of equipartition of the energy. As a matter of fact, Planck's quantum hypothesis arises from his adoption of the second alternative, and a denial of the validity of equipartition in the case of vibratory motion. The principle of equipartition was first deduced in connection with the kinetic theory of gases. Now even in this original and limited sphere the principle does not stand on absolutely undebatable foundations. A great deal depends on the interpretation of the meaning to be attributed to the word "average". It is usually assumed that the average condition, say, of a molecule, is a "time" average; the sum of successive values of a quantity connected with the molecule, over a long period of change in the system, divided by the number of such values.

But it is doubtful if the principle of equipartition based on such an interpretation of the word "average" is really proved at all by dynamical principles. The point is fully treated by Jeans in his *Dynamical Theory of Gases*. It would appear that the "average" really referred to is an average extended over all conceivable conditions or "complexions" of a system (excepting a negligible number) and not merely over such conditions or "complexions" through which the system passes on any particular "path". The extension to "time" average cannot be made unless by the introduction of Maxwell's assumption of "continuity of path," *viz.* that the system will in process of time pass through all conceivable "complexions". This assumption is of doubtful validity, and is known to be unsound in certain of the problems treated in general dynamics, *e.g.* the periodic orbits of astronomy (a type of vibratory motion).

To proceed, Planck, denying the applicability of equipartition to radiation theory, works out from special considerations (to be dealt with presently) that in the vibratory motion obtaining in wave-trains, each degree of freedom corresponding to a frequency ν should possess on the average not kT ergs of kinetic and potential energy, but an amount—

$$\frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}} - 1} \text{ ergs}$$

(where h is a new universal constant, determined by experiment to be approximately $6{\cdot}55 \times 10^{-27}$). If we make use of the Rayleigh-Jeans calculation of the degrees of freedom, we find that the energy-density of the radiation in the range ν, $\nu + \delta\nu$ is—

$$\frac{8\pi}{c^3}\cdot\frac{h\nu^3}{e^{\frac{h\nu}{kT}}-1}\cdot\delta\nu \text{ ergs per c.c.,}$$

or in terms of wave-lengths—

$$\frac{8\pi ch}{\lambda^5}\cdot\frac{1}{e^{\frac{ch}{k\lambda T}}-1}\cdot\delta\lambda \text{ ergs per c.c}$$

These expressions agree remarkably well with the most recent measurements, for all values of ν or λ, enabling the calculation of h to be made with some precision.[1]

It is only natural that, in adopting a more or less revolutionary attitude to a principle hitherto enjoying the confidence of the scientific world, Planck and his followers should have modified somewhat the original presentation of their ideas to meet the various criticisms urged by those who seek to retain the traditional standpoint. It is well known that Planck himself has receded somewhat from the position adopted in his earlier papers on the subject. This position is fully expounded in the first (1906) edition of his book, *Theorie der Wärmestrahlung* (Leipzig, Barth); the later form of his theory is contained in *Deutsch. Phys. Gesell. Ver.*, **13**, 3, 138, 1911, or in the second (1913) edition of the above book. Einstein's speculations and applications are to be found in various papers in the *Annalen der Physik* from 1905 onwards.

It is impossible to reproduce the whole of Planck's line of argument here, but the following brief account will bring out the essentially novel principle introduced by him, and serve also to show to some extent why and how he receded from the earlier to the later position.

He remarks that any radiating mechanism of frequency ν, placed in a temperature enclosure, will acquire an average energy depending on the energy-density of the radiation of that frequency in the enclosure. The radiating mechanism of which he avails himself is an electric doubtlet, consisting of an electrified particle vibrating harmonically under the attraction of an oppositely electrified nucleus to which it is held by a force of the usual elastic, proportional-to-the-displacement type. In the enclosure there exist a great number N of these doublets or "oscillators," having their axes fixed in a certain direction, *i.e.* endowed with one degree of freedom. By an application of the usual equations of the electro-magnetic field, he shows that—

$$U(\nu)=\frac{8\pi\nu^2}{c^3}L(\nu) \quad . \quad . \quad . \quad . \quad (1)$$

where $L(\nu)$ is the mean energy (kinetic and potential) of an oscillator and $U(\nu)\cdot\delta\nu$ is the energy-density of the radiation in range ν to $\nu+\delta\nu$. Of course if we put $L(\nu)$ equal to kT, as usual, we would arrive as before at the Rayleigh-Jeans Law. Planck, however, avoids this by assuming that his oscillators can only emit and absorb discontinuously,

[1] *La Théorie du Rayonnement* (Gauthier-Villars, 1912), pp. 78-92.

and that at any instant the energy of an oscillator can only be an integral multiple of a finite unit or "quantum" of energy, the amount of the unit depending on the frequency. It is to be carefully noted that this does not imply, of necessity, an atomic structure for energy—a view, indeed, repudiated by Planck; it does imply that the oscillator must emit or absorb whole quanta of radiation at one time (at present, be it noted, we are discussing Planck's earlier views). Now such an assumption necessarily involves a modification of Maxwell's distribution law, for that law depends on the possibility of the infinite divisibility of the energy among the oscillators, atoms, molecules, and so forth. The point is more easily followed with aid of a "condition-diagram". Suppose we denote the charges of the doublets as $\pm e$, the mass of the vibrating particle as m, and x as its displacement along its axis at time t, then the equation of its "free" motion is—

$$\ddot{x} + 4\pi^2\nu^2 . x = 0$$

or

$$m\ddot{x} + 4\pi^2\nu^2 . mx = 0$$

where ν is the frequency. If X is the resolved component of the electric intensity of the field along x at time t, the equation of its forced motion is—

$$m\ddot{x} + 4\pi^2\nu^2 mx = eX \quad . \quad . \quad . \quad . \quad (2)$$

If we denote the energy of the particle by ϵ—

$$m\dot{x}^2 + 4\pi^2\nu^2 mx^2 = 2\epsilon,$$

or denoting its momentum by $y(=m\dot{x})$—

$$\frac{y^2}{m} + 4\pi^2\nu^2 m . x^2 = 2\epsilon \quad . \quad . \quad . \quad . \quad (3)$$

Now the condition of any oscillator as regards the displacement and momentum of its vibrating particle can be clearly represented on a plane diagram by a point with co-ordinates x and y. All those oscillators whose energy is ϵ have their representative points lying on the ellipse—

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

where

$$a^2 = \frac{\epsilon}{2\pi^2\nu^2 . m},$$

and

$$b^2 = 2\epsilon m.$$

The area of this ellipse is of course πab, *i.e.* $\frac{\epsilon}{\nu}$.

The history of any oscillator can be represented by the motion of a point on this diagram, travelling along a curve, passing outward from the origin when the energy of the oscillator is increasing, and inwards when the energy is decreasing. Maxwell's Law states that the number of oscillators whose displacements and momenta lie between the limits x, y, and $x + \delta x$, $y + \delta y$ is—

$$A . e^{-\frac{\epsilon}{k\tau}} dxdy \text{ (A being a constant).}$$

If we integrate this over the narrow ring in the diagram between two ellipses determined by values of the energy ϵ and $\epsilon + \delta\epsilon$, we have for the number of oscillators whose energies lie between ϵ and $\epsilon + \delta\epsilon$, the expression—

$$Ae^{-\frac{\epsilon}{kT}}\delta\epsilon/\nu.$$

Of course, on the assumption of infinite divisability of the energy, the total number of oscillators, N, should be—

$$\frac{A}{\nu}\int_0^\infty e^{-\frac{\epsilon}{kT}}d\epsilon.$$

But the essence of Planck's idea is that this integral should be replaced by a convergent series. For, according to his ideas, the representative points can only be found on the ellipses corresponding to energies $\epsilon_1, \epsilon_2, \epsilon_3 \ldots \epsilon_n$, etc., where ϵ_1 is the quantum of energy and $\epsilon_n = n \cdot \epsilon_1$; they will lie nowhere between these ellipses. The points will, as it were, jump from ellipse to ellipse. The areas of these ellipses are of course—

$$\frac{\epsilon_1}{\nu}, \frac{\epsilon_2}{\nu}, \frac{\epsilon_3}{\nu}, \text{ etc., or } \frac{\epsilon_1}{\nu}, 2\frac{\epsilon_1}{\nu}, 3\frac{\epsilon_1}{\nu}, \text{ etc.,}$$

and the various rings between them have all a common area. It is a feature of Planck's theory that he gives this area a constant value for all oscillators of any period, and denotes it by the letter "h," so that—

$$\epsilon_1 = h\nu,$$
$$\epsilon_2 = 2h\nu,$$
$$\epsilon_3 = 3h\nu, \text{ etc.}$$

The integral expression N above must now be replaced by the series—

$$\begin{aligned} N &= \frac{A}{\nu}\left[e^{-0}\cdot\epsilon_1 + e^{-\frac{\epsilon_1}{kT}}(\epsilon_2 - \epsilon_1) + e^{-\frac{\epsilon_2}{kT}}(\epsilon_3 - \epsilon_2) + \text{etc.}\right] \\ &= \frac{A}{\nu}\left[h\nu + e^{-\frac{h\nu}{kT}}h\nu + e^{-\frac{2h\nu}{kT}}h\nu + \ldots\right] \\ &\quad - Ah\left[1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\right] \\ &= Ah\frac{1}{1 - e^{-\frac{h\nu}{kT}}} \quad \ldots\ldots\ldots\

$$= e^{-\frac{h\nu}{kT}} \frac{A h^2 \nu}{\left(1 - e^{-\frac{h\nu}{kT}}\right)^2}$$

$$= \frac{N h\nu \cdot e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}}$$

$$= \frac{N h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore L(\nu) = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad (6)$$

By equation (1) it follows that—

$$U(\nu) = \frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad (7)$$

an equation which agrees well with observed results, if, as has already been noted, h is put equal to $6{\cdot}55 \times 10^{-27}$. It should be evident now that Planck escapes from the Rayleigh-Jeans conclusion entirely by his hypothesis of discontinuity in the exchanges of energy between the oscillators and the medium. Had he assumed that ϵ_1, $\epsilon_2 - \epsilon_1$, $\epsilon_3 - \epsilon_2$, etc., are infinitesimally small, he would have found for $L(\nu)$ in (6) the limit of the right-hand expression as $h\nu$ approaches zero, which is just kT, and so have arrived back at equipartition and the previous discrepancy. His essential point is, in fact, the assumption that h is finite, *i.e.* that the "elementary region of the condition diagram" has a finite size. So that in a sense Planck's theory is more an innovation in the method of probabilities, and need not be confined to radiation problems. This point will be touched on later.

Two obvious criticisms of this first line of argument have been advanced. First, equation (1) is obtained by an application of electromagnetic equations which rest on the assumption of a continuous exchange of energy between oscillators and medium. But as Campbell in his *Modern Electrical Theory* (2nd edition) points out, this may not be a fatal flaw in the reasoning. Maxwell's equations may be quite true for average values of the electric and magnetic quantities involved without implying their absolute validity at all instants in the immediate neighbourhood of one oscillator, and so equation (1) might still stand as an equality of average values, even though the discontinuity assumed by Planck existed for individual doublets and their near environment. It should be noted, however, in passing, that at a high temperature, say 2000° C., the quantum of energy for high-grade light of the order $\nu = 10^{15}$ is 30 times as large as the average energy of an oscillator in these conditions.

The second objection is that to produce the enormously great number of qualities which are known to exist in complete radiation, we

should have to postulate the existence of a very great number of oscillators of different frequencies. Now, all the evidence which we possess on the nature of atomic structure negatives such a view, nor is there any real evidence that any vibrating electron in an atom emits simple harmonic waves at all. Indeed, one of the outstanding difficulties of the Planck theory is just this difficulty of formulating a plausible physical basis for it.

There is a further difficulty awaiting us when we seek to apply the notion of discontinuous absorption to the phenomena of ejection of electrons from the surfaces of bodies on which is incident a beam of ultra-violet light (the photo-electric effect), or a pencil of X-rays. All the evidence favours the view that a definite amount of energy has to be at least resident in the electron before it can be ejected. In the normal photo-electric effect the energy of the electron after escape is found to have a maximum value $h'\nu - w$, where ν is the frequency of the incident light, h' a constant whose value agrees fairly closely with Planck's h, and w is a constant characteristic of the metal from which the electrons are escaping. A quite plausible hypothesis is that $h'\nu$ represents the amount of energy in the electron before its escape; of this it loses an amount w in leaving the atom against restraining forces which depend on the particular structure of the atom; and so, if it is on the surface and has not to part with still more energy in escaping from the influence of neighbouring atoms, it would retain an amount $h'\nu - w$ after emergence. Now this appears to fit very well indeed with Planck's original assumption of the discontinuous and sudden absorption of a quantum $h\nu$, which, if ν is large enough, would supply the necessary energy for the escape of the electron from those atoms which the laws of chance brought at any definite instant into the suitable condition for absorption. But there seems to be this fatal objection to such a simple hypothesis, that the photo-electric effect has been observed *without any delay* in cases where the intensity of the light, as calculated by the inverse square law and on the assumption of continuous propagation through the ether, could not have possibly supplied the necessary quantum to an electron in a molecule or atom in less than 10 or 15 minutes. Similar difficulties arise in connection with the secondary β-rays caused by X-rays, if one considers the energy of the X-ray pulse as uniformly distributed throughout the pulse. In fact, if one adheres to the hypothesis of discontinuous absorption, one must admit that the energy of any beam of radiation is not uniformly diffused throughout the space occupied by the beam. This is indeed roughly the manner in which Einstein escapes from the difficulties. He has advanced the view that the energy of light is itself atomic in structure, and absorption and emission are of necessity discontinuous, not because of the special structure of the oscillators, etc., but because of the nature of light itself. His view is, in reality, a quantum of *energy* view; it has already been observed that Planck's is not necessarily so; indeed Planck dissociates himself at present from so revolutionary a hypothesis. It is noteworthy that J. J. Thomson had already been led to speculations somewhat

similar to Einstein's, by considerations based on his hypothesis of Faraday tubes in the ether emanating from charged particles.[1] It should be noted that Thomson's view of a "filamental" structure in the ether might well be expected to lead to a different result for energy-density than that reached by Rayleigh and Jeans; for their calculation of the degrees of freedom in the ether, it will be recalled, depends on taking the ether as a perfectly continuous medium. Such a view would indeed be more like the adoption of the first of the alternatives referred to previously as methods of escape from the Rayleigh-Jeans discrepancy. In reference to such views, it must be admitted that, however useful they may be for the immediate purpose of overcoming such difficulties as those connected with the photo-electric effect, and X-rays, and however well they suit the needs of radiation formulæ, they involve a return to the corpuscular theory of light, a raising of all the old difficulties of accounting for diffraction and interference on such a theory, and at present they lack a system of fundamental postulates, such as those on which stands the present edifice of dynamics and electro-dynamics. Of course, there is no gainsaying that the construction of such a system may be attempted and may be successfully carried out, and Newtonian dynamics placed in the position of a good approximation to truth, but without absolute validity.

As has been already suggested, Planck meets these difficulties in a less revolutionary fashion; he abandons the hypothesis of discontinuous absorption, retaining discontinuous emission. By so doing he meets fairly successfully (though not entirely, as I hope to show presently) the objection lodged against his method of obtaining equation (1). His new hypothesis concerning his oscillators is that they can emit only at definite instants, *viz.* when they contain an integral number of quanta, $h\nu$. If they contain any fraction of a quantum over an integral number they cannot radiate. When radiation does take place it is "catastrophic," *i.e.* it cannot cease until the whole energy of the oscillator has been lost. The particular number of quanta possessed by an oscillator when it radiates are determined by the laws of chance, the chance of its reaching a given number being less the greater the number and the smaller the radiation-density. In fact, Planck's new line is based on three postulates:—

(*a*) In any finite time the total emission equals the total absorption.

(*b*) For small frequencies (*i.e.* long wave-lengths), the quanta of energy are so small that emission is practically continuous, and the ordinary dynamical and electro-dynamical laws are a good approximation to the facts even for individual oscillators and their immediate neighbourhood.

(*c*) The chance of a particular oscillator emitting when arriving at a "critical" state (*i.e.* containing an integral number of quanta) is less the stronger the field. In particular, the chance of no emission taking place to the chance of an emission is a ratio proportional to the radiation-density.

[1] *Electricity and Matter* (Constable, 1904). *Phil. Mag.*, **19**, 301, 1910.

Concerning these, (*a*) is clearly a statement of fact in a state of equilibrium; (*b*) is a justifiable hypothesis, inasmuch as the Rayleigh-Jeans formula is suitable for experiments on long wave-lengths. As regards (*c*), the first part of it is plausible enough, but the particular statement of it in the second sentence appears to be an *a posteriori* assumption, based on the necessity of arriving at a formula (already experimentally proven) by the method employed.

To proceed to a brief outline of his new analysis, Planck replaces equation (1) by another giving the rate of absorption of an individual oscillator in a field of given radiation-density. With the same notation as before, he finds on the basis of equation (2) (taken to be valid for continuous absorption) that—

$$\frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} U(\nu) \quad . \quad . \quad . \quad . \quad (8)$$

As the right-hand expression is clearly positive, the equation refers to an increase of the oscillator energy, *i.e.* absorption.

Adopting the same geometrical representation of the condition of an oscillator as before, the history of an oscillator is not represented now by the leaping of a point from one to another of the "critical" ellipses corresponding to the energies, $h\nu$, $2h\nu$, $3h\nu$, etc. Its behaviour follows the continuous movement of a point from the origin outwards, and a jump back to the origin when the point reaches some one of the "critical" ellipses (the particular one being a matter of chance), the outward journey being once more resumed. The number of oscillators is as before given by—

$$N = A\hbar \frac{1}{1 - e^{-h\nu/kT}} \quad (4)$$

but the equation (5) for E must be altered. The energy of any oscillator is no longer, at any instant, an integral number of quanta; all amounts can exist, and the average energy of an oscillator whose representative point is known to lie in a particular ring must be taken as the mean of the energies corresponding to the elliptical boundaries of the ring, *i.e.* it must be an integral number of quanta plus half a quantum. On this basis it is easy to show that (5) must be replaced by—

$$\dot{E} = \frac{N h\nu}{e^{h\nu/kT} - 1} + \frac{N h\nu}{2} \quad . \quad . \quad . \quad . \quad (9)$$

and therefore—

$$L(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \quad . \quad . \quad . \quad . \quad (10)$$

on the average.

Of course we cannot apply equation (1) to this; that has been discarded, and replaced by (8); but before proceeding further it may be as well to remark that Planck's new hypothesis enables him to account for the photo-electric effect taking place without delay, even for weak light; for obviously there are at any instant a number of oscillators just

within an infinitesimally small amount of energy from arrival in a "critical" state, and of these a portion will radiate almost instantaneously, or eject an electron. Thus Planck avoids Einstein's revolutionary postulate on the atomicity of energy.

We saw above that the number of oscillators whose energy lies between ϵ and $\epsilon + \delta\epsilon$ is—

$$Ae^{-\epsilon/kT} \cdot \frac{\delta\epsilon}{\nu},$$

and so the number whose representative points lie between the nth and the $(n + 1)$th ellipse is $Ahe^{-(n+\frac{1}{2})h\nu/kT}$; the number whose points are in the next ring are $Ahe^{-(n+\frac{3}{2})h\nu/kT}$. That is, of all those which acquire an amount of energy between $nh\nu$ and $(n + 1)h\nu$, the fraction $e^{-h\nu/kT}$ pass the $(n + 1)$th "critical" state and acquire an amount of energy between $(n + 1)h\nu$, and $(n + 2)h\nu$. So $e^{-h\nu/kT}$ is the chance of no emission taking place, and therefore $1 - e^{-h\nu/kT}$ is the chance that an emission will take place. By postulate (c) above, we have—

$$\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \rho U(\nu),$$

where ρ is a constant to be determined, *i.e.*—

$$\rho U(\nu) = \frac{1}{e^{h\nu/kT} - 1} \quad . \quad . \quad . \quad . \quad (11)$$

therefore by equations (8) and (10)—

$$\rho h\nu \frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$= \frac{\pi e^2}{3m}\left(L(\nu) - \frac{h\nu}{2}\right) \quad . \quad . \quad . \quad (12)$$

Now for small values of ν, $\frac{h\nu}{kT}$ is small and $L(\nu)$ approaches the value kT, $h\nu$ being therefore negligible in comparison with $L(\nu)$; so for *small values* of ν—

$$\rho h\nu \frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} L(\nu) \quad . \quad . \quad . \quad . \quad (12a)$$

Now Hertz has shown that in this case (for here by postulate (b) the classical methods are applicable) the rate of emission of a vibrating electric doublet is equal to the fraction $\frac{8\pi^2\nu^2e^2}{3c^3m}$ of its own energy.[1] But in equilibrium the rate of emission is equal to rate of absorption, therefore Hertz's result gives us for our case—

$$\frac{dL(\nu)}{dt} = \frac{8\pi^2\nu^2e^2}{3c^3m} \cdot L(\nu).$$

[1] *Wied. Ann.*, **36**, p. 12, 1889.

and so by (12*a*)—

$$phv = \frac{c^3}{8\pi v^2}$$

or

$$p = \frac{c^3}{8\pi h v^3}$$

and therefore by (11) we obtain once more—

$$U(v) = \frac{8\pi}{c^3} \frac{hv^3}{e^{hv/kT} - 1}.$$

Planck has thus succeeded in obtaining his radiation formula once more, but with the help of a rather artificial postulate (*c*), and also by ignoring the fact that his adoption of the electro-magnetic equations necessarily implies a continuous radiation from his vibrating electric particle. Such a particle in its excursions backwards and forwards along an ever-increasing amplitude must of necessity have a motion which is not uniform, but now accelerated, now retarded, and must during such variations of its motion be radiating; at least, that is the logical conclusion from traditional views. As a matter of fact, in a series of interesting papers in the *Phil. Mag.*, dealing with the line-spectra of the elements, Bohr frankly admits this point, but makes a most ingenious use of it, taking the first step, in fact, towards a system of dynamics with which the behaviour of such systems as Planck's oscillators would harmonise.[1]

It is doubtful if Planck's work would ever have received the consideration bestowed on it, had it not happened that an ingenious application of it by Einstein to the problem of specific heats initiated a remarkable series of researches, theoretical and experimental, which showed the hypothesis of discontinuity was fruitful of good results in other branches of physics and chemistry than radiation. It is well known that while high-grade radiation is exchanged by some mechanism which is sub-atomic in nature (vibrating electrons for instance), infra-red "heat" radiation is emitted and absorbed by means of the atoms and molecules as a whole. Einstein's idea was that in a monatomic *solid* each atom has a definite frequency of vibration, which, he assumed, can be determined by optical methods (the "residual ray" method of Rubens, for instance, or dispersion-formulæ). If $L(v)$ is the expression used previously, each atom has on the average an amount of energy $L(v)$ for each degree of freedom, that is, $3L(v)$ altogether, on the basis of Planck's work, extending to "infra-red atom" oscillators. Hence if there are N atoms per gram-atom in the body, the atomic heat of the body would be $3NL(v)$ or $\frac{3Nhv}{e^{hv/kT} - 1}$. A differentiation of this expression with respect to T would give the specific heat at the temperature T (for constant volume). The result is—

[1] *Phil. Mag.*, July, September, November, 1913; March, 1914.

$$C_v = 3Nk \frac{x^2 e^x}{(e^x - 1)^2};$$

where $x = \frac{h\nu}{kT}$. If x is small, *i.e.* if ν is small or T large, this expression approaches the value $3Nk$, which is known to be 5·95 calories, and is indeed the Dulong-Petit value of the atomic specific heat. For small values of T, however, x is large and the above expression grows smaller and smaller, ultimately approaching the limit zero as T approaches zero or x approaches infinity. That is, there should be a gradual decrease to zero of the specific heat of a solid as the temperature approaches absolute zero. This was known to be true in a general way. Further, as C is a function of $\frac{\nu}{T}$, the curves connecting specific heat and temperature for various monatomic solids should be similar. In fact, for two solids whose atomic frequencies are ν_1 and ν_2, the curve for the second would be obtained from the curve for the first by maintaining the same ordinates (representing C) and altering all the abscissæ (representing T) in the ratio $\nu_1 : \nu_2$. A series of now famous researches were undertaken by Nernst and his pupils; details of the work will be found in papers in the *Ann. der Phys.*, p. 395, 1911, in the *Zeitsch. für Electrochem.*, 1911 and 1912, in the *Théorie du Rayonnement*, and in Nernst's four lectures delivered at University College, London, on the solid state. The similarity of the curves was proved, while Einstein's actual expression, although following the general course of the change in specific heat with the temperature, exhibited considerable numerical discrepancies, especially at low temperatures. Nernst and Lindemann proposed an alternative formula—

$$C = \frac{3}{2} Nk \left[\frac{x^2 e}{(e^x - 1)^2} + \frac{\left(\frac{x}{2}\right)^2 \frac{x}{e^2}}{\left(e^{\frac{x}{2}} - 1\right)^2} \right].$$

This, although in good agreement with results, was a piece of lucky guesswork, founded on no solid theoretical basis. In a paper in the *Ann. der Phys.*, **39**, p. 789, 1912, Debye attacked the problem from a broad standpoint, and his result, from its agreement with experiment and the soundness of its premises, seems to have approached finality in this domain.

Debye points out that there can be no single "characteristic" vibration of the atoms of a monatomic solid. There are an enormous number of such vibrations; they constitute an "acoustic" spectrum; they are the fundamental and overtones of the body considered as emitting a note. A knowledge of the elastic constants of the material is sufficient to determine them, just as Rayleigh and Jeans determined the frequencies possible in a cubical "block" of ether. For these

vibrations constitute waves of "sound" travelling through the body with definite speeds. There are, for instance, "distortional" transverse waves travelling with a velocity v_1, and "compressional" longitudinal waves travelling with a velocity v_2. v_1 can be calculated if one knows the density ρ and modulus of rigidity μ of the material; it is in fact $v_1 = \sqrt{\frac{\mu}{\rho}}$; v_2 can be calculated if one knows in addition the bulk-modulus K—

$$v_2 = \sqrt{\frac{K + \frac{4\mu}{3}}{\rho}}.$$

Now, the number of degrees of freedom for vibrations having frequencies between ν and $\nu + \delta\nu$ is, as previously, $\frac{8\pi}{v_1^3}\nu^2\delta\nu$ per unit volume for the transverse waves, and $\frac{4\pi}{v_2^3}\nu^2\delta\nu$ for the longitudinal. (N.B.—The factor 8π occurs because the transverse waves are polarisable in two rectangular planes, the longitudinal are not.) Consequently the whole modes of vibration per unit volume between ν and $\nu + \delta\nu$ are $\left(\frac{8\pi}{v_1^3} + \frac{4\pi}{v_2^3}\right)\nu^2\delta\nu$. We saw above that the similar formula developed for the ether by Rayleigh and Jeans suffered from the drawback that, in integrating it, no finite upper limit could be assigned on account of the assumed continuity of the ethereal medium. In this case, however, there must be a finite upper limit to ν, because the number of degrees of freedom cannot exceed $3N$ for a gram-atom of the substance.

Hence if ν_m is the highest frequency possible—

$$3N = \left(\frac{8\pi\tau}{v_1^3} + \frac{4\pi\tau}{v_2^3}\right)\int_0^{\nu_m}\nu^2 d\nu$$

(where τ is the volume of a gram-atom)

$$= \left(\frac{8\pi\tau}{3v_1^3} + \frac{4\pi\tau}{3v_2^3}\right)\nu^3{}_m$$

$$= F\nu^3{}_m$$

where F is a constant calculable from the elastic constants and density of the body.

Since $\nu_m = \left(\frac{3N}{F}\right)^{\frac{1}{3}}$, ν_m is also calculable. For Al, Cu, Zn, Ag, Pb, Diamond it is of the order 10^{12} to 10^{13}. Now by ascribing, according to the extension of Planck's work, the energy—

$$\frac{h\nu}{e^{h\nu/kT} - 1}$$

to every degree of freedom, we obtain for the energy-content of body due to wave-motion of frequencies ν to $\nu + \delta\nu$—

$$3\mathrm{F} \cdot \frac{h\nu^3\delta\nu}{e^{h\nu/k\mathrm{T}} - 1},$$

or

$$\frac{9\mathrm{N}}{\nu_m^3} \cdot \frac{h\nu^3\delta\nu}{e^{h\nu/k\mathrm{T}} - 1}.$$

Hence the total energy—

$$= \frac{9\mathrm{N}}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{exp\frac{h\nu}{k\mathrm{T}} - 1}$$

$$= \frac{9\mathrm{N}k\mathrm{T}}{x^3} \int_0^x \frac{y^3 dy}{e^y - 1}$$

where $x = \frac{h\nu_m}{k\mathrm{T}}$, and $y = \frac{h\nu}{k\mathrm{T}}$.

A differentiation of this expression with regard to T produces this expression for the specific heat at constant volume—

$$\mathrm{C} = 3\mathrm{N}k\left[\frac{12}{x^3}\int_0^x \frac{y^3 dy}{e^y - 1} - \frac{3x}{e^x - 1}\right].$$

This is clearly a function of x or $\frac{h\nu_m}{k\mathrm{T}}$, and therefore suitably accounts for the similarity of the specific heat curves of different solids. Further, the expression agrees remarkably well with determinations of Nernst and his co-workers, more so in fact if ν_m is calculated not from the values of elastic constants, but from a formula discovered by Lindemann,[1] connecting ν_m and the melting point (taking ν_m as the frequency of vibration of an atom under the influence of its neighbours). The computation is not easily carried out, for the integral in the above expression cannot be evaluated in finite terms, and so one has to resort to the summation of series which can be obtained to suit various ranges of temperature as regards their convergency. One striking result emerges from the calculation, *viz.* that at very low temperatures the specific heat varies as the cube of the absolute temperature; this would appear to be true to within 1 per cent. for the range of temperature 0° to $\frac{h\nu_m}{12k}$.

Nernst has made a very happy combination of Einstein's and Debye's formulæ in the treatment of diatomic solids such as KCl,

[1] *Physikalische Zeitschrift*, 11, 609 (1910).

NaCl, AgCl, KBr, and the triatomic substance $PbCl_2$. He supposes the heat content of the body to be constituted of two parts, one due to the vibrations of the molecules as a whole, and the other to the vibrations of the atoms within the molecules. The first part can be obtained by Debye's method, taking the upper limit of the frequency as determined by Lindemann's melting-point formula; the second part can be determined by Einstein's method, the characteristic frequency being determined by Rubens' "residual rays" method. The agreement with observation is quite good; details can be found in *Vorträge uber die Kinetische Theorie der Materie und der Elektrizität* (Teubner). Still further extensions of Debye's ideas have been made by Born and Kármán and Thirring in papers contained in the *Phys. Zeit.*, 14 (1913).

It was pointed out above that Planck's formula is derived from an innovation in the treatment of statistical problems, the assumption, in fact, that the elementary region of the two-dimensional condition diagram for a system of oscillators is finite in area, and the replacement of Maxwell's integral by a series. Planck has applied the same idea to the six-dimensional condition diagram for an ideal monatomic gas, and arrived at a result which had been already obtained by Nernst, who bases his derivation of it on his well-known "heat theorem".[1] There are several ways of wording this theorem, according to the particular thermodynamic function which one elects to make use of in the statement. As expressed by Planck in his *Thermodynamics*, it is as follows: "The entropy of a condensed system, which is chemically homogeneous, is zero at the absolute zero of temperature". This law removes from the expression for the entropy of a body in a definite state that indefiniteness in value which arises in the usual thermodynamic treatment and which is due to the entrance into the formula of an undetermined constant on integrating the differential of the entropy. For clearly if the entropy of a body can be given definitely for one state, it is determinate for all other states which can be conceivably reached from the former by a reversible path. So if we can conceive that the body can be led to the condition of a chemically homogeneous solid or liquid at absolute zero, by a reversible process, Nernst's heat theorem makes it possible to calculate its entropy without ambiguity, if sufficient experimental data are available. By such means it can be shown that the entropy of one gram-molecule of an ideal gas is given by the equation—

$$S = C_p(1 + \log T) - R \log p + a \quad . \quad . \quad (13)$$

(absolute units of temperature, pressure, and energy being used), where the "chemical constant," a, indeterminate on pure thermodynamical grounds, has, according to Nernst's theorem, the value—

$$R \log \left(\frac{p}{\theta^{\frac{5}{2}}}\right) + \frac{r_0}{\theta} \quad . \quad . \quad . \quad . \quad (14)$$

in which p_s is the vapour pressure of liquid condensed from the gas at a very low temperature θ, and r_0 is the heat of vaporisation of the liquid at absolute zero.

[1] *Nachr. d. Ges. d. Wissensch zur Göttingen Math. Phys. Kl.* (1906).

Planck arrives at this result on dynamical grounds in the following manner. Conceiving a monatomic gas as an aggregate of particles with three effective degrees of freedom, and representing the co-ordinates of a particle by x, y, z, and its velocity components by u, v, w, the condition diagram is a six-dimensional one in which the position and momentum of a point representing a particle are given as x, y, z, mu, mv, mw (m being the mass of a molecule). According to the Maxwell Law the number of molecules whose representative points lie within the limits x, y, z, mu, mv, mw, and $x + dx \ldots m(w + dw)$ is—

$$\mathrm{N}A e^{-\frac{\epsilon}{k\mathrm{T}}} dxdydzdudvdw \qquad . \quad . \quad (15)$$

where N is number of molecules in a gram-molecule, ϵ the energy of a molecule in condition xyz, u, v, w, due to its position and velocity, and A is a number given by the equation—

$$1 = \mathrm{A}\int e^{-\frac{\epsilon}{k\mathrm{T}}} dxdydzdudvdw.$$

If one puts $\epsilon = \frac{1}{2}m(u^2 + v^2 + w^2)$, it follows that—

$$\mathrm{A} = \frac{1}{\mathrm{V}} \left(\frac{m}{2\pi k\mathrm{T}}\right)^{\frac{3}{2}}$$

V being the volume of the gas.

Now, according to Planck's view, instead of the differential element of the six-dimensional diagram which occurs in (15), we ought to introduce a finite element having a value G, definite in size for a system of definite molecules. The form and position of these "elementary regions" would, as in the two-dimensional case, be bounded by the "surfaces" or loci of equal energy. If we number these regions 1, 2, 3, . . . n, we can say that a fraction f_1 of the representative points lie in region 1, etc., f_n in region n, where—

$$f_n = \mathrm{A} \cdot e^{-\frac{\epsilon_n}{k\mathrm{T}}} \cdot \frac{\mathrm{G}}{m^3}$$

ϵ_n being the molecular energy corresponding to the nth region. With this notation, it is possible to express the entropy of the gas, as Boltzmann has shown (see his *Gastheorie*, or Jeans' *Dynamical Theory of Gases*), in the form—

$$\mathrm{S} = -k\mathrm{N}\Sigma f_n \log f_n.$$

Of course in Boltzmann's treatment, as in Maxwell's, f_1, f_2, etc., are infinitesimally small, since the differential element $dxdydzdudvdw$ occurs instead of $\frac{\mathrm{G}}{m^3}$, and so the expression for S contains a constant of indeterminate (and infinite) value. By assuming G to be finite, Planck avoids this conclusion, just as he avoids the Rayleigh-Jeans law in radiation, by assuming h to be finite and not infinitesimally small. He finds, by using the value given above for A and f_n, that—

$$S = kN\left[\log \frac{V(2\pi mkT)^{\frac{3}{2}}}{G} + \frac{E}{NkT}\right]$$

where E is the kinetic energy of the molecules.

Writing R for k. N and putting E equal to $\frac{3}{2}RT$, we obtain—

$$S = R\left[\frac{3}{2}(1 + \log T) + \log V + \frac{3}{2}\log (2\pi mk) - \log G\right]. \quad (16)$$

Since $pV = RT$ and $c_p = \frac{5}{2}R$, equation (13) can be readily transformed to—

$$S = R\left[\frac{3}{2}(1 + \log T) + \log V - \log R + \frac{a}{R} + 1\right]. \quad (17)$$

The formal similarity between (16) and (17) is obvious, and the two results lead to the connection between Planck's G and Nernst's "chemical constant," a, given by the equation—

$$\frac{3}{2}\log (2\pi mk) - \log G = -\log R + \frac{a}{R} + 1,$$

or—

$$G = \frac{R(2\pi mk)^{\frac{3}{2}}}{e^{\frac{a}{R}+1}}.$$

The thermodynamic treatment can be found in the third edition of Planck's *Thermodynamics*, Chap. VI. The development of the ideas based on the quantum hypothesis is given in his *Theorie der Wärmestrahlung* (2nd edition, pp. 110-32).

APPENDIX III.

Krüger's Theory of Gyroscopic Molecules.

[This appendix represents the substance of two papers by F. Krüger, *Annalen Physik*, [iv.], **50**, 346; *ibid.*, **51**, 450 (1916), on "The vibrations of free gyroscopic molecules," and on "Molecular precessional vibrations and specific heat."]

Maxwell pointed out that a magnet must behave as a gyroscope if the ampere molecular stream (the origin of magnetisation) be of a material nature, and he carried out an experiment to decide this point with an electromagnet, without, however, finding the expected result. The electron theory has referred the ampere (magnetic) current to rotating electrons. But the electrons possess mass, and therefore their circulatory motion gives to the molecule containing them a certain angular momentum. O. W. Richardson (*Phys. Rev.*, **26**, 248, 1908) showed in the case of a freely hanging magnetised iron wire that, owing to the angular momentum N of the molecules, a torsion must manifest itself, although he was unable at first to obtain a definite result owing to experimental difficulties. Recently Einstein and J. W. de Haas (*Verh. d. D. phys. Ges.*, **17**, 152, 203 (1915)) have succeeded in giving an exact calculation of the torsion which the wire should experience, and have also succeeded in overcoming the great experimental difficulties. They have in fact employed their method to calculate the ratio of the charge to the mass of an electron. Further, S. J. Barnett (*Phys. Rev.* [ii.], **6**, 239 (1915)) has shown that magnetic effects can be produced in an iron wire by rapid rotation of the wire. Also Maxwell's original experiment has been taken up again by W. J. de Haas and by G. L. de Haas and Lorentz (*Proc. K. Akad. Wetenschap.*, **24**, 398 (1915)), who have shown that the effect can scarcely be expected to be experimentally detectable. The gyroscopic characteristics and properties of the atoms of metallic iron due to the existence of molecular currents, *i.e.* the rotations of electrons in the atoms, can now be considered to be definitely demonstrated.

In addition to magnetic investigations there have sprung into existence in the last few years certain optical theories in connection with the laws of line spectra which have rendered very probable the existence of rotating electrons even in the case of those molecules whose magnetic character is by no means pronounced. Such electron planetary systems have formed the basis of the atomic models of Rutherford and of Nicholson. Based on such, Bohr has constructed a model atom by

bringing in the quantum theory which not only accounts for the series laws but also quantitatively for the Rydberg constant in terms of the Planck constant h, the charge e, and the mass μ of the electron. According to Bohr, one or more electrons rotate round the nucleus of an atom in a fixed path with the angular momentum $h/2\pi$ or a whole multiple thereof, the different angular momenta corresponding to rotations of the electrons in paths of different diameter. This theory has been applied with success by Warburg (*Verh. d. D. phys. Ges.*, **15**, 1259 (1913)) to explain the Stark electrical effect. Recently Debye has employed a similar atomic model to calculate the dispersional properties of hydrogen in particular. The general dispersion formula has been given by Sommerfeld (*Elster and Geitel Festschrift*, p. 549 (1915)).

If these models correspond to reality, it follows that such atoms, and, as a special case, the hydrogen molecule, must possess gyroscopic properties. In the following treatment it will be shown that the gyroscopic properties of gaseous molecules, in particular the hydrogen molecule, are of considerable importance for the theory of gases, especially in connection with the problem of molecular heat of gases, and are capable of solving certain difficulties which exist at the present time.

On Bohr's theory the hydrogen molecule consists of two positively charged hydrogen nuclei with two electrons rotating round the line joining the centres of the nuclei, each electron possessing an angular momentum of $h/2\pi$. The hydrogen molecules behave therefore as small gyroscopes, which are at the same time free from forces such as gravity, for the gas is almost perfect. What is particularly significant from the standpoint of kinetic theory is *the behaviour of such molecular gyroscopes under collisions.*

The translational motion of such freely moving molecules, each with three degrees of freedom, is naturally the same whether the molecules possesses gyroscopic properties or not. But we have now to consider the nature of the remaining degrees of freedom which must be attributed to the molecule in order to account for its molecular heat. There are at least two degrees of freedom to be accounted for. These, as has been pointed out in Chapter IV., have been ascribed by Bjerrum to rotation of the molecule as a whole. But, as Krüger goes on to say, according to the fundamental equations of gyroscopic theory, a gyroscope *cannot* carry out any *rotations*, but it *can* be put into a state of vibration which, in the case of a symmetrical gyroscope free from external forces —the case here considered—corresponds to regular precession, *i.e.* precessional vibrations. Krüger's theory consists in substituting the idea of precessional[1] vibrations of the atoms in place of rotation of the molecule as a whole, in order to account for the two remaining degrees of freedom. The advantage of this comes in, as we shall see later, in connection with monatomic molecules. In the case considered the precessional vibration of the atoms is regarded as due to a vibration of each electron perpendicular to its own orbit whilst it still keeps on fol-

[1] See the footnote on p. 23 of Chap. I.

lowing the orbit as its "average" path. Krüger points out that according to gyroscopic theory the angular velocity of regular precessional vibrations is—

$$\nu = \frac{C \cdot \psi'}{A - C} \cdot \frac{1}{\cos \phi}$$

where C is the moment of inertia of the electron round the figure-axis, *i.e.* the axis joining the centres of the two atomic nuclei together, A is the moment of inertia of the atom nucleus perpendicular to the figure axis, and ϕ denotes the angle swept out by the figure axis as a result of the precession. Further—

$$\psi' = \frac{d\psi}{dt}$$

where ψ' is the angular velocity of a rotating electron or rate of spin of the electron. The angle ϕ depends naturally upon the vibrational energy and the temperature. For low temperatures and molecules with very small moments of inertia, as is probably the case with the hydrogen molecule ϕ will be small, and we can make the usual approximation that since ϕ is small $\cos \phi = 1$. Hence we obtain—

$$\nu = \frac{C\psi'}{A - C}.$$

The product in the numerator, *viz.* $C\psi'$, represents the angular momentum N of the electron spin so that we can write—

$$\nu = \frac{N}{A - C}.$$

The angular velocity of the precession is thus directly proportional to the angular momentum of the spin of the electrons. Further ν is greater the smaller the denominator, that is, the more closely the moments of inertia A and C approach one another, that is, the more spherical the gyroscope. For a spherical gyroscope A = C and ν = infinity.

It is to be remembered that in the molecular gyroscope the precessional vibrations are brought about as a result of collisions with other molecules. In the case of the hydrogen molecule the two hydrogen atoms or nuclei are enclosed by the path followed by the two electrons, this path being fixed by the electrostatic and centrifugal forces. The moment of inertia C is here that of the two electrons which rotate or spin at a distance r round the figure-axis of the molecule.

The important conclusion now arrived at is that those molecules which possess rotating electrons do not themselves rotate but carry out vibrations of the precessional kind which are independent of temperature, or nearly so. The two atoms at either end of the figure-axis follow a small circular path as a result of the precessional "wobble" of the electrons.

The vibration of regular precession of symmetrical bodies possesses the characteristic of having two degrees of freedom, each of which represents kinetic energy but no potential energy. The hydrogen

molecule possesses therefore in all five degrees of freedom as on the older theory. It will be observed that Krüger does not take into account any vibration of the nuclei with respect to one another along the path or figure-axis joining their centres. Calling the molecular heat C_v, then, in the region of temperature in which the equipartition principle holds, it follows that C_v is given by the relation—

$$C_v = 5R/2 = 4{\cdot}96.$$

It will be recalled that the molecular heat of hydrogen in the neighbourhood of 0° C. is 4·9 to 5·2 cals., whilst at 2000° abs. it is of the order 6·5 cals.

Krüger further points out that the two degrees of freedom which correspond to the precessional vibrations can be treated from the quantum standpoint just as in the analogous case of the vibrations of a solid: that is, the energy content decreases with falling temperature and converges to zero at zero temperature. A marked decrease in energy content with lowering of temperature has been shown experimentally to be the case with hydrogen by Eucken (*Sitzungs. Akad. Wiss.*, Berlin, 1912, p. 14 (*cf.* Chap. IV.)). The curve obtained by Eucken for the molecular heat points to a single frequency independent of the temperature.

For the special case of the hydrogen molecule in which the optical properties yield quantitative values for the gyroscopic properties, the angular velocity of precession may be calculated and compared with that obtained from the specific heat data. For this purpose it is necessary to use the numerical values which Bohr has calculated for the constants of the hydrogen molecule (*Phil. Mag.*, [vi.], **26**, 487, 1913 (*cf.* Chap. V.)). For the angular momentum of a single rotating electron, $\mu r^2\psi'$ (where r = the radius of the electron's path, ψ' = the angular velocity of its rotation, and μ the electronic mass), we have the value—

$$h/2\pi = 1{\cdot}06 \times 10^{-27}.$$

For the radius r of the electron's path Bohr finds the value $\frac{1{\cdot}10}{2} \times 10^{-8}$ cm.,

and for ψ' the value $3{\cdot}86 \times 10^{16}$ per second. [The latter quantity is just $2\pi\omega$, where ω has been defined in Chapter V. as the frequency of revolution of the electron, and possesses the value $6{\cdot}2 \times 10^{15}$ for the electron of the hydrogen *atom*. Bohr has shown (*cf.* Chap. V.) that, for the electrons of the hydrogen *molecule*, ω is 1·1 times the ω for the single electron of the atom. We should therefore employ a slightly greater value for ψ' than that adopted by Krüger.] Further, Bohr has calculated that $2d$, the distance apart of the two atoms, is $0{\cdot}635 \times 10^{-8}$ cm., the mass of the atom having the value $1{\cdot}64 \times 10^{-24}$ gram, the mass of the electron being $8{\cdot}97 \times 10^{-28}$ gram. It follows therefore that A, the moment of inertia of the atoms perpendicular to the figure axis, is $2 \times 1{\cdot}64 \times 10^{-24} \times (0{\cdot}317 \times 10^{-8})^2$ or $3{\cdot}30 \times 10^{-41}$. Similarly moment of inertia, C, of the two electrons is given by—

$$2 \times 8{\cdot}97 \times 10^{-28} \times (5{\cdot}52 \times 10^{-9})^2 \text{ or } 5{\cdot}43 \times 10^{-44}.$$

C can therefore be neglected compared with A. Hence for the angular velocity of precession we have—

$$\nu = h/2\pi A = \frac{1{\cdot}06 \times 10^{-27}}{3{\cdot}30 \times 10^{-41}} = 3{\cdot}21 \times 10^{14}.$$

The angular velocity ν of precessional vibration is related to the *frequency* ν' of precessional vibration in a very simple manner, *viz.*—

$$\nu' = \nu/2\pi.$$

Hence $$\nu' = \frac{\nu}{2\pi} = \frac{3{\cdot}21 \times 10^{14}}{6{\cdot}28} = 5{\cdot}11 \times 10^{12}.$$

This expression is obtained by equating the angular momentum to $h/2\pi$. This, however, only holds for a single electron. Hence for the two electrons of the hydrogen molecule we get just twice the value for ν'—

$$\nu' = 1{\cdot}006 \times 10^{13}$$

(revised value given in Krüger's second paper).

Thus, with the help of Bohr's results, *i.e.* results in agreement with the optical properties of the hydrogen molecule, Krüger has obtained a value for the vibrational frequency exhibited by the molecule in virtue of precessional vibrations. We have now to see how far this value is borne out by a consideration of the molecular heat of hydrogen. Eucken has applied the quantum theory to the problem of the molecular heat of hydrogen in the simple form originally suggested by Einstein for the case of solids, *i.e.* we have to do with a single vibration frequency which ought to agree with the value of ν' obtained above, if Krüger's argument is correct.

The formula employed by Eucken is—

$$C_v = R.\frac{\left(\frac{\beta\nu'}{T}\right)^2 \times e^{\beta\nu'/T}}{(e^{\beta\nu'/T} - 1)^2}.$$

To make this agree with observed values it is necessary to write $\beta\nu' = 430$, and, since $\beta = 4{\cdot}86 \times 10^{-11}$, it follows that $\nu' = 8{\cdot}85 \times 10^{12}$. The agreement between the two values for ν' is satisfactory.

The equation obtained by Krüger on the basis of the gyroscopic theory of the molecule has also been obtained by Nernst (*Verh. d. D. phys. Ges.*, **18**, 83, (1916)) based on quite different considerations, involving rotation of the molecule. Nernst points out that in the case of hydrogen a more correct value for $\beta\nu'$ is 450, whence ν' is $9{\cdot}3 \times 10^{12}$. This agrees even more closely with the value obtained by Krüger on the basis of precessional vibrations.

The above considerations hold good, naturally, not only for hydrogen but for all gas molecules in which rotating electrons exist, and, according to Bohr, the series spectra, which are a general property of gases, are due to such rotating electrons. The diminution of approximately 5 per cent. in the molecular heats of nitrogen and carbon monoxide between 273° and 90° abs. observed by K. Scheel and W. Heuse (*Ann.*

Physik, **40**, 473, (1913)) is also, according to Krüger, to be referred to precessional vibrations, which are obeying the quantum principle of energy distribution as a function of temperature. Krüger's conclusions may be summed up as follows:—

Since, in general, we may expect all molecular systems to possess rotating electrons, we may say that in the case of molecules which contain two or more atoms such molecules do not exhibit rotation as a whole, but on the other hand exhibit precessional vibrations on account of their gyroscopic properties. The number of degrees of freedom on this view remains the same as on the older view of rotations.

It has already been pointed out that the molecular heats lead us to the conclusion that in the ordinary range of temperature a diatomic gas has five and not six degrees of freedom. That is, one of the expected degrees is missing. Krüger points out that the ordinary rotation theory does not give any satisfactory explanation of why there is one degree of freedom missing. By making use of the precessional vibration idea the fact that five degrees are possessed is self-evident, for precessional vibration gives rise to two degrees of freedom (purely kinetic), and the free translation of the molecule gives rise to three degrees of freedom also purely kinetic. It will be observed that Krüger is not considering the vibration of the ordinary kind of the two atoms with respect to one another. Further, in the case of a monatomic gas we have seen that the inertia terms A and C approximate to one another with the result that the frequency of precession becomes exceedingly great, and in the limit when the molecule is spherical it becomes infinite. Hence monatomic molecules are unable, according to the quantum theory, to take up any sensible amount of energy over the temperature ranges hitherto examined, for the only kind of radiant energy which such a system would be capable of picking up would be that belonging to the extreme ultra-violet region. That is, the monatomic gases, such as mercury, argon, etc., do not possess any internal energy as far as their molecular heats are concerned; the molecular heat is completely taken account of by the three degrees of freedom of translation of the molecule as a whole. This explanation of the behaviour of monatomic gases is one of the main advantages of Krüger's theory.

In the second of the papers cited Krüger goes on to consider in more detail the question of the infra-red spectra of gases in relation to the concept of precessional vibrations.

It has been shown experimentally by Rubens and Wartenberg (*Verh. D. phys. Ges.*, **13**, 796 (1911)) that the elementary gases such as H_2, O_2, Cl_2, Br_2, which are electrically neutral structures, show no absorption in the infra-red region between 23 and 314μ, whilst on the other hand the markedly electrically-polar gases, such as HCl, HBr, and H_2O, possess strong absorption over this range. This fact has hitherto been ascribed to the rotations of the dipoles, for rotating dipoles must emit and absorb radiant energy. According to Bohr's atomic model as extended by W. Kossel (*Ann. Physik*, **49**, 359 (1916)), these

dipoles are surrounded by a swarm of rotating electrons which no longer occupy a position in the middle of the figure-axis, but are displaced towards one end. It follows that these molecules must possess gyroscopic properties, and cannot rotate, but experience precessional vibrations. The infra-red bands referred to would correspond therefore to precessional vibrations and not to rotations. [Note that the infra-red bands produced by the "ordinary" vibration of atoms with respect to one another (in a manner analogous to the vibration of atoms in solids) occur in the short infra-red region, *viz.* 2 to 5μ. We are at present dealing with bands in the much further infra-red.] In general both ideas, rotation and precessional vibration, lead to the same results; a distinction does indeed exist, *viz.* the position of the absorption band on the basis of precessional vibration should be practically independent of the temperature, whilst in the case of rotations the position should be displaced towards the shorter wave-length region as the temperature rises. Direct measurements upon this point are wanting.

An indirect test of the question is possible, however. Lord Rayleigh (*Phil. Mag.*, [v.], **24**, 410 (1892)) has calculated that a linear oscillator, vibrating with frequency ν_0 and rotating with frequency ν_1 must radiate or absorb at the three frequencies, ν_0, $\nu_0 + \nu_1$, and $\nu_0 - \nu_1$. As a rule ν_1 is small compared with ν_0. If, instead of rotation, we substitute precessional vibration with frequency ν_1, exactly the same frequencies should be brought into play; their intensities will, however, be altered.

Rayleigh's considerations have been applied by Bjerrum (*Nernst Festschrift*, 1912, p. 90; *Verh. d. D. phys. Ges.*, **16**, 640, 737 (1914)) to explain the infra-red absorption spectra of gases. He points out that an absorption band in the short wave part of the infra-red spectrum, which is due to linear vibrations, must be split into three owing to rotation of the molecule. In this way he has explained the broadening of the 3·5μ line of HCl, the broadening of the infra-red lines of CO_2, and the splitting of the 5·9μ band of water vapour, as due to rotational frequencies existing in the far infra-red region. [The rotational frequency repeats itself, as it were, close to a true vibrational frequency, the rotational frequency being separated from the central vibrational frequency by the small quantity $\pm \nu_1$.]

The absorption bands in the short infra-red region have been measured very accurately by Burmeister (*Verh. d. D. phys. Ges.*, **15**, 589 (1913)) and by E. von Bahr (*ibid.*, 731, 1150 (1913)), who found that, in general, *double* bands are characteristic of this part of the spectrum, which would correspond to the theory of Bjerrum provided one assumes, as does E. von Bahr that, on account of insufficient dispersion, the middle sharp line does not appear.

The distance of the two decomposition bands must depend on temperature on account of the variation of the rotational frequency with the temperature—that is, assuming that rotation is the cause of the phenomenon. On the other hand, this distance should be practically

independent of the temperature if it be due to precessional vibrations. According to von Bahr the product $\lambda_r \times \sqrt{T}$ is a constant, where λ_r is the rotational wave-length and is given by—

$$\lambda_r = \frac{2\lambda_1\lambda_2}{\lambda_1 - \lambda_2}$$

when λ_1 and λ_2 are the two wave-lengths of the double-headed band.

von Bahr's relation is to be expected if a rotation accompanied by the amount of energy assumed on the classical mechanics were present (*cf.* Chap. IV.). It is to be remarked at the same time that with very energetic precessional vibrations the angle ϕ swept out by the axis as a result of precessions becomes greater, so that cos ϕ cannot any longer be set equal to unity. This will naturally occur at high temperatures. In fact, the smaller the angular momentum compared with the difference of the moments of inertia A and C of a symmetrical gyroscope, the more closely do precessional vibrations approximate to rotations.

It is fairly clear from an examination of the infra-red spectrum that in the case of water vapour we are not dealing with a rotation obeying the laws of classical statistical mechanics. Beyond 9μ approximately it shows a series of absorption bands with constant wave-length difference; on the shorter wave side of 9μ it shows a number of bands symmetrically placed with respect to the band at $6{\cdot}24\mu$. Bjerrum considers the first group, *i.e.* those beyond 9μ as single rotation frequencies in the sense of the quantum theory; those on the shorter side of 9μ as the "decomposition" bands brought about by the interaction of the $6{\cdot}24\mu$ band with each of the rotational bands. As a matter of fact, the measurements of Rubens and Hettner (*Verh. d. D. phys. Ges.*, **18**, 154 (1916)) show that such a relation exists between the lines under and beyond 9μ. The Rayleigh formula corresponds very closely to the frequencies observed by Rubens and Hettner between 9 and 200μ. To regard these long wave-lengths as due to rotations in the sense of the original quantum theory is, however, not very satisfactory. The original expression of Bjerrum, with a constant frequency difference of $1{\cdot}73 \times 10^{12}$ gives far too few lines, so that Eucken introduced a second series with a frequency difference of $0{\cdot}75 \times 10^{12}$, which accounts for the majority of the missing bands, though not for all (*cf.* Chap. IV.).

We have now to consider the spectrum of water vapour from the standpoint of the precessional vibrations. Krüger has employed the Bohr model for the atom or molecule, and it will be remembered that the angular momentum may not only be $h/2\pi$ but also twice, thrice, etc., this value. These different angular momenta correspond to different frequencies, which, since C is negligible compared with A, correspond to twice, thrice, etc., the fundamental vibration frequency. We would expect therefore, on Krüger's theory, series of bands inter-related. Krüger, however, considers it doubtful whether these simple considerations could give rise to a sufficiently great number of bands, for the Bjerrum series is 20 and that of Eucken 40.

It must be pointed out, however, that the water molecule is not a

symmetrical gyroscope. Owing to this lack of symmetry more complex relations are to be expected. In the case of an asymmetric gyroscope with three different moments of inertia, we find in place of the regular precession of the figure-axis describing a circular path on a surface, the more complicated form of the general Poinsot vibration. Such movement possesses three degrees of freedom as the molecular heat of water vapour requires. In the case of the water molecule the electrons do not all revolve in the same plane. These new modes of motion and interaction may be expected to give rise to a number of bands so that the spectrum of water vapour would be expected on these grounds to be complex. There is a further point. The measurements of Rubens and Hettner have shown that the bands are fairly broad. This is not easy to reconcile with the Bjerrum rotation theory. The breadth of the bands is attributed by Krüger to certain of the molecules which possess a value for the angle ϕ which is far from the mean value.

If we consider the difficulties which surround the application of the quantum theory to rotation frequencies, it would appear that precessional movement with complex vibrational form is the more plausible hypothesis. Possibly an intensive examination of the dependence upon temperature of the wave-lengths of rotation bands, together with a complete discussion of the form of vibration of the water molecule, might serve to decide between the two views.

The Quantity ϕ.

The general equation for the frequency of the precessional vibrations is, as we have seen—

$$\nu' = \frac{N}{2\pi A} \cdot \frac{1}{\cos \phi} \quad . \quad . \quad . \quad . \quad (1)$$

For small values of ϕ the cosine term becomes unity. Krüger now considers more closely the question of the calculation of ϕ. The angle ϕ is defined by the movement of the atom (in the hydrogen molecule) which describes a circle of radius ρ with a velocity v. If m be the mass of the atom the precessional energy of both atoms (or of the whole molecule) is $mv^2 = E$ Now, $v = 2\pi\rho\nu'$ and $\rho = a \sin \phi$, where a is the distance of an atom from the middle point of the figure-axis. Hence $v = 2\pi a\nu' \sin \phi$.

Therefore $mv^2 = 4\pi^2 ma^2\nu'^2 \sin^2 \phi = 2\pi A^2\nu'^2 \sin^2 \phi$
where A stands for $2ma^2$.

Further $2\pi^2 A\nu'^2 \sin^2 \phi = E \quad . \quad . \quad . \quad . \quad (2)$

or $\sin^2\phi = E/2\pi^2 A\nu'^2 \quad . \quad . \quad . \quad . \quad (3)$

From equation (1) we have—

$$\cos^2 \phi = \frac{N^2}{4\pi^2 A^2} \cdot \frac{1}{\nu'^2} \quad . \quad . \quad . \quad . \quad (4)$$

From equations (3) and (4) we get—

$$\tan^2 \phi = \frac{\sin^2 \phi}{\cos^2 \phi} = \frac{2EA}{N^2}$$

or
$$\tan \phi = \frac{\sqrt{2EA}}{N} \quad . \quad . \quad . \quad . \quad (5)$$

It follows that we can write $\cos \phi$ in the form—

$$\cos \phi = \frac{N}{\sqrt{N^2 + 2EA}} \quad . \quad . \quad . \quad . \quad (6)$$

If we denote by ν'_0 the value of ν' when $\cos \phi = 1$, we get—

$$\cos \phi = \nu'_0/\nu' \quad . \quad . \quad . \quad . \quad . \quad (7)$$

a formula which may be easily introduced into (6).

In order to make $\cos \phi = 1$ it is necessary, from equation (6), to have $2EA$ small compared with N^2. This condition will be favoured by a small moment of inertia A, and by a small value for the energy of precessional movement; this corresponds to moderately low temperatures.

If we eliminate ϕ from equations (3) and (4) we obtain the precessional vibration frequency as a function of the energy. Thus we find—

$$p\nu'^2 = E + \frac{N^2}{2A} \quad . \quad . \quad . \quad . \quad (8)$$

where p is written for $2\pi^2 A$.

Since
$$\nu'_0 = \frac{N}{2\pi A},$$

we have
$$\nu'^2 = \frac{E}{p} + \nu'^2_0$$

or
$$E = p(\nu'^2 - \nu'^2_0) \quad . \quad . \quad . \quad . \quad (9)$$

If we calculate, as do Einstein and Stern (*Ann. Physik*, **40**, 551 (1913)) with a mean value for the vibration frequency ν' at a given temperature T, we find for the energy of the precessional movement of a molecule the expression—

$$E = \frac{h\nu'}{e^{h\nu'/kT} - 1} \quad . \quad . \quad . \quad . \quad (10)$$

and hence
$$\nu'^2 = \frac{1}{p} \cdot \frac{h\nu'}{e^{h\nu'/kT} - 1} + \frac{N^2}{2Ap} \quad . \quad . \quad . \quad (11)$$

This equation allows us to calculate ϕ from equations (6) or (7) for each value of ν' corresponding to a given temperature. Krüger gives a table for the temperature range $T = 0°$ to $T = 300°$. The following is a selection from Krüger's values:—

T.	ν'.	Cos ϕ.	ϕ.	$C_{prec.}$
0	$1{\cdot}0055 \times 10^{13}$	1·000	0	0
67·5	1·0060	0·9995	2° 45′	0·036
79·5	1·0070	0·9986	3°	0·159
103·1	1·010	0·9956	5° 21′	0·385
157·8	1·028	0·9781	12°	0·871
299·6	1·110	0·9059	25° 3′	1·38

The last column denotes that part of the molecular heat which is due to the precessional vibrations, *i.e.*—

$$C_{prec.} = dE/dT = \frac{dE}{d\nu'} \cdot \frac{d\nu'}{dT}.$$

It will be observed that the change in the mean vibration frequency ν' due to the increase in the precessional energy amounts at 100° to about 0·5 per cent., whilst at 300° it is not quite 10 per cent.

Krüger considers alternative modes of calculation of the molecular heat of hydrogen at considerable length, for which the reader is referred to the original paper.

Behaviour at High Temperatures.

Let us return to the expression—

$$\cos \phi = \frac{N}{\sqrt{N^2 + 2EA}}.$$

We have already considered the case in which 2EA is small compared with N^2. As the temperature is raised, however, E increases, so that cos ϕ diminishes and the frequency ν' increases. At very high temperatures 2EA may be very large compared with N^2. Under these conditions we have—

$$\cos \phi = N/\sqrt{2EA}.$$

and for the vibration frequency—

$$\nu' = \frac{N}{2\pi A} \frac{1}{\cos \phi} = \frac{1}{\pi \sqrt{2}} \cdot \sqrt{\frac{E}{A}}.$$

Since, on the basis of the equipartition principle, which holds at high temperatures, we can write $E = kT$, we have for the vibration frequency of precession—

$$\nu' = \frac{1}{\pi \sqrt{2}} \cdot \sqrt{\frac{k}{A}} \cdot \sqrt{T}. \quad . \quad . \quad . \quad (12)$$

The frequency is thus proportional to the square root of T; *under these conditions the precessional movement has become a true rotation whose vibration frequency is given by the same formula.* The conclusions may therefore be summed up as follows: Molecules, to which their revolving

electrons give gyroscopic properties, possess, at low temperatures and with small values for the moment of inertia (A), a vibration frequency which is nearly independent of temperature; with rising temperature the frequency increases, and, at high temperatures, if the product $2EA$ exceeds N^2, the precessional movement passes into a true rotation. In the case of hydrogen, if we put $E = kT$, then $2EA = N^2$ at $T = 489°$; that is, the gyroscopic angular momentum N is still sensible; it is only at much higher temperatures that hydrogen is capable of giving rise to true rotations, as a result of molecular collisions.

In the case of molecules which possess moments of inertia A larger than that of hydrogen, the transformation of precessional vibration into true rotations occurs at correspondingly lower temperatures. Thus it is very probable that the increase in distance apart of the double bands of water vapour at $\lambda = 6{\cdot}512\mu$ and $\lambda = 5{\cdot}948\mu$, which Paschen has observed (*Ann. Physik*, **52**, 215 (1894)), is due to the *rotational* character of the motion, since, according to E. von Bahr (*Verh. d. D. phys. Ges.*, **15**, 731, 1150 (1913)), the product of the rotation wave-length λ_r (defined by $\lambda_r = \frac{2\lambda_1 \times \lambda_2}{\lambda_1 - \lambda_2}$) into $\sqrt{T}$ is approximately a constant (*cf.* Chap. IV.).

On the other hand, the double bands which E. von Bahr has observed in the short infra-red spectrum of carbon monoxide are characterised by the fact that their distance apart, *i.e.* the quantity λ_r, is only very slightly affected by temperature change over the range 15 to 145° C. The quantity λ_r in this case is regarded by Krüger as being the wave-length characteristic of true precessional vibration, and it is conceivable, as Krüger points out, that on raising the temperature still further, the distance apart of the double bands, *i.e.* the quantity λ_r, would then show a definite temperature effect. Under such conditions we would be observing the change from precessional vibrations into true rotations.

As regards the question of molecular heats, the chief point of interest lies in the departure from the principle of equipartition at low temperatures, and here the precessional vibrations of the molecules with a certain gyroscopic moment of inertia possess the character of vibrations with constant period.

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